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OTTAWA, CANADA

CANADIAN JOURNAL OF RESEARCH

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THE EFFECT OF ALTERNATING ELECTRICAL FIELDS ON THE POLYMERIZATION OF STYRENE[1]

BY W. A. BRYCE,[2] C. A. GENGE,[3] AND C. A. WINKLER

Abstract

Equipment for studying the effects of alternating fields on chemical reactions is described. The catalyzed polymerization of liquid styrene was investigated, with fields of frequencies ranging from 1.15 to 7.72 Mc. and with field strengths up to 4500 v. per cm. The rate of polymerization was reduced by the application of the fields, the inhibition increasing approximately as the square of the voltage. The fields appeared to have a greater inhibiting effect on the oxygen-catalyzed than on the benzoyl peroxide – catalyzed reaction. Varying the frequency over the above range had no effect on the amount of inhibition caused by the field. At all temperatures, catalyst concentrations, voltages, and frequencies, the fields had no significant effect on the viscosity-average molecular weight of the polymer.

Introduction

Modern theories of chemical reactions suggest that the reactivity of molecules is governed by the distribution of electrical charge in groups and bonds, and that this distribution may be altered by changes in the electrostatic environment of the molecule (15). Electronic distortions of this type are believed to be induced by the electrical fields of attacking groups. It has been established that the application of an electrical field can cause a significant polarization of a dielectric (5). It may therefore be possible to affect a chemical reaction in some way by altering the electron distribution in molecules through the application of a suitable electrical field.

Several investigations of this type have been undertaken, but because of differences in characteristics of the fields used a direct comparison of the results obtained is not always valid. In two studies in which unidirectional fields of the order of 10,000 v. per cm. were used no effect was observed on the nitration of benzoic acid or on the addition of hydrogen bromide to 2-pentene (3). D-c. fields with potential gradients of the order of 13.5 kv. per mm. also had no effect on the polymerization of styrene (11).

[1] *Manuscript received in original form February 27, 1948, and, as revised, November 16, 1949.*

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.

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The effects of alternating fields have been studied for a variety of chemical systems. In some investigations, fields of high frequency and indeterminate strength were used, and in others high potential gradients were applied at low frequencies.

High frequency alternating fields have been reported to promote such reactions as the esterification of acetic acid with ethanol (7), the liberation of iodine from aqueous sodium iodide (23), the formation of formaldehyde from methane and carbon dioxide, and the polymerization of ethylene to oily products (8). The polymerization of acetylene and ethane and the decomposition of ethanol, amyl alcohol, and diethyl ether by the action of high frequency fields has been reported (14). The effect of alternating fields on the rate of combustion of acetylene–air mixtures was found to be frequency-dependent, changing from a retardation at frequencies less than 10 Mc. to an acceleration at higher frequencies (16).

Liechti (11) studied the effect of 50-cycle fields, with strengths up to 50 kv. per mm., on the rate of polymerization of liquid styrene. At a critical potential gradient of 43.5 kv. per mm. the polymerization was accelerated. At higher potentials the acceleration was reduced and the rate approached that of the thermal polymerization. Styrene treated initially in a high tension field polymerized more rapidly than untreated styrene, when both were polymerized thermally; the activation persisted for periods of over a week. In a similar investigation but with much lower field strengths Medvedchuk (13) observed only an activation of styrene polymerization.

An increase in the rate of polymerization of styrene (17) and chloroprene (22) has been observed as a result of the application of microwaves.

In many of the investigations reported above, no allowance was made for the effect of dielectric heating occurring in the system as a result of applying the alternating field. This heat is believed to be a measure of the work done in displacing electrical centers and rotating dipoles in the dielectric (19). The dependence of the dielectric heating, H, on the applied frequency, f, the voltage gradient, E, and the dielectric constant D, is given by the relation:

$$H = KfE^2D,$$

where K is a constant characteristic of the medium and of the units used. The reliability of results obtained in rate studies in which estimates of temperature variations were not made may be open to question.

The present investigation was undertaken to determine whether the rate of a chemical reaction can be influenced by a suitable applied electrical field, careful account being taken of temperature changes caused by dielectric heating.

The polymerization of styrene was selected as the chemical reaction to be studied in the present investigation, since the results of previous investigators

indicated that this reaction could be influenced in some way both by fields of high potential gradient and by high frequency radiations. In addition, the low dielectric constant (2.486) (9) and low dipole moment make styrene suitable as a dielectric owing to its minimal effect on cell capacitance, and because of the small amount of dielectric heating that should occur in it. The temperature coefficient for the polymerization of styrene is only 1.45 (4) and hence the reaction rate should not be unduly sensitive to slight temperature irregularities occasioned by incompletely controlled dielectric heating.

Experimental

Reagents

The styrene used was obtained from the Polymer Corporation at Sarnia, Ont. It was distilled in the presence of an inhibitor, tertiary butyl catechol, at 25°C. and approximately 10 mm. pressure, and was stored in a dark brown bottle for not more than two days prior to use. The benzoyl peroxide used as a catalyst was of analytical reagent grade made by Eastman Kodak Co., Rochester, N.Y. C.P. grade benzene and methanol were used where these reagents were required.

Description of Equipment

A diagram of the apparatus is presented in Fig. 1. The source of the alternating field was a 60 w. Marconi TW-12 transmitter operating in the frequency range 1.147 to 10.03 Mc. The unit was very stable during operation, as moderate changes in load had no significant effect on the frequency of the oscillator circuit.

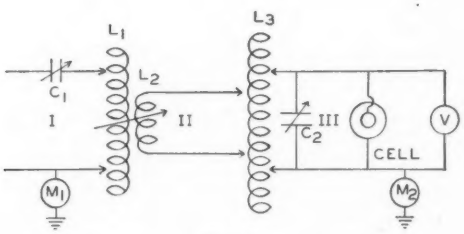

FIG. 1.

Power from the transmitter was conveyed to the reaction cell circuit through a link stage. The link was coupled to the transmitter by a variable inductance, L_2, which moved inside L_1, a large inductance in the aerial tank circuit of the transmitter. Variable coupling was necessary at this stage to obtain maximum energy transference at each frequency. The link was tapped into the center of a large autotransformer, L_3, in the reaction cell circuit. The portion of L_3 between the two taps was the primary, and the rest of the coil was the secondary of the transformer. For the lower frequencies L_3 was wound on a Pyrex coil form 2 1/4 in. in diameter and 15 in. long, and consisted of 195 turns of No. 18 gauge double-cotton covered copper wire. The turns ratio

between secondary and primary was generally about 50 to 1. Taps were placed at intervals along the coil to permit variation of both primary and secondary sections. As the frequency was increased, a smaller inductance in L_3 was required for tuning the capacitance in the circuit.

The other components of the reaction cell circuit were: a variable condenser, C_2, for tuning to resonance; the condenser-reaction cell, which had an r.f. milliammeter between it and ground; and a vacuum tube voltmeter for measuring the potential developed across the cell. C_2 was a 10 $\mu\mu$f. transmitter condenser.

The reaction cell (Fig. 2) was in the form of a cylindrical condenser with a partially hemispherical lower end. It was of glass construction throughout with the exception of the metal electrodes. The two parts of the cell were joined

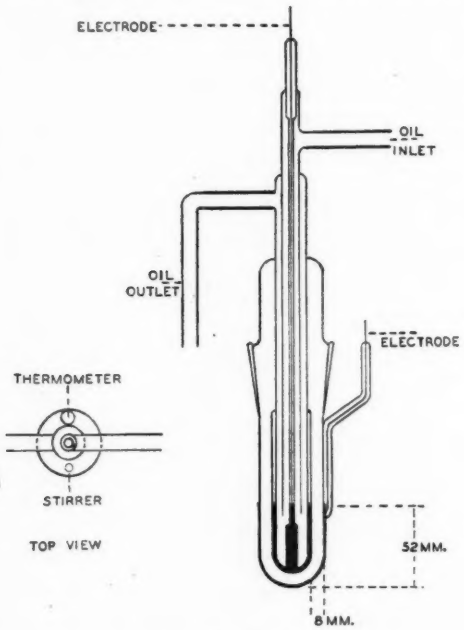

FIG. 2.

by a 50/50 S.T. ground-glass joint. The upper portion supported the inner electrode, which consisted of a film of mercury (1 mm. thick) between two concentric glass tubes. The high potential was applied to this electrode by means of a silver lead extending up through a fine tubing in the center of the cell. The inner electrode was so constructed that bath oil could be circulated through it to aid in the dissipation of heat produced in the dielectric by the field. The lower part of the cell supported the outer electrode, which was made

of thin silver foil cemented to the outer surface of the glass tube. It was connected to ground by a copper lead extending through a glass side arm. Both connections to the cell were made as short as possible to minimize inductive and capacitive effects.

The condenser portion of the cell was 52 mm. high, 36 mm. wide and had a volume of 40.5 ml. Its capacitance, when filled with pure styrene, was 7.7$\mu\mu$f. The space occupied by the liquid was 8 mm. in thickness throughout. Adequate stirring was maintained with a fine glass stirrer extending through a close-fitting tube in the upper portion of the cell. The top of the cell also supported a thermometer well through which a calibrated thermometer extended into the reaction mixture. An alcohol thermometer was used for measuring the temperature of the liquid in the field, in accordance with reliable commercial practice (21). However, it was found that the observed temperature rise resulting from dielectric heating was independent of the nature of the thermometer.

The voltage developed across the cell was measured with a vacuum tube voltmeter (A. W. Barber Laboratories, Flushing, N.Y.) with a specially constructed multiplier probe. This instrument had a capacity of 5 $\mu\mu$f., and permitted voltage measurements up to 10,000 v. at radio frequencies, with an error of not more than 5%.

The potential developed in the reaction cell circuit could be varied readily by changing the coupling between coils L_1 and L_2, and could be set at any value within the power limits of the transmitter. The voltage was also very sensitive to sharp tuning by means of variable condenser C_2. The maximum potential obtained across the cell with styrene as the dielectric was 5300 v. at 1.55 Mc. This maximum decreased with increasing frequency owing to the reduced power output of the transmitter. No attempt was made to compensate for this loss by the use of amplifiers.

The transmitter was calibrated for frequency with a precision wavemeter (Type 224 L, Gen. Radio Co., Cambridge, Mass.).

Methods

In most of the experiments a catalyst, benzoyl peroxide, was used to ensure that the reaction would proceed at a suitable rate. The addition of known amounts of the peroxide also served to minimize the relative catalytic effect of oxygen (6, 10, 18, 20).

A standard procedure was used for all experiments. The benzoyl peroxide was dissolved in freshly distilled styrene, and 40.5 ml. of the reaction mixture was placed in each of two similar cells, one of which served as a control, the other as a field cell. The reaction was started by heating the cells in a thermostat for a definite period of time. This prefield thermal treatment was used to ensure that the two samples were polymerizing at the same rate when the

field was applied to one of them. The field cell was placed in the bath 15 min. ahead of the control to stagger the sampling, and to make it easier to adjust the control temperature to follow the field cell temperature at all times.

At the end of this initial polymerization period, during which time from 10 to 15% of the monomer was converted to polymer, the field cell was placed in a second bath at the same temperature as the first. The thermostatic system in the latter bath was so arranged that bath oil circulated through the inner electrode of the cell. The high frequency circuits were then connected to this cell, and the field was applied. The temperature of the reaction mixture immediately rose several degrees owing to dielectric heating. The extent of the temperature rise is shown in Fig. 3 for a typical experiment. After a steady-state temperature was reached no significant variation occurred. The temperature of the control cell was carefully adjusted to compensate for dielectric heating in the field. The temperature difference between field and control cells was rarely greater than 0.2°C.

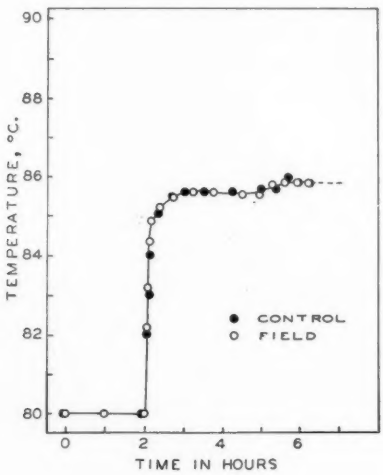

FIG. 3.

The course of the reaction was followed by gravimetric determination of the amount of polymer formed (per cent conversion). A sample of approximately 1.5 gm. was obtained by removing the thermometer and inserting a pipette into the reaction mixture through the thermometer well. The weighed sample was dissolved in 10 ml. of benzene containing a trace of hydroquinone (inhibitor), and the polymer was precipitated by the addition of 50 ml. of methanol. The monomer styrene, benzene, and methanol were distilled off at 65°C. under vacuum, and the polymer was dried to constant weight.

To determine what effect, if any, the conditions of the experiment might have on the degree of polymerization of styrene, the average molecular weight

of the polymer was determined, using the standard viscometric method (2, p. 1003).

Four variables were considered in this investigation: field strength (volts per centimeter); field frequency; reaction temperature; and catalyst concentration. The experiments were accordingly divided into three series in each of which one or two of the factors were varied while the remainder were held constant.

Series I: Variation of Catalyst Concentration and Voltage at Constant Temperature and Frequency

The catalyst concentration was varied from zero to 2.182 gm. benzoyl peroxide per liter, using field strengths of 1500, 3000, and 4500 v. per cm. at 1.55 Mc. The initial or base temperature selected was 80°C. A two hour prefield heating period was used in all these experiments except those at low catalyst concentrations, where the initial heating was extended so that the reaction mixture would be exposed to the field at approximately the same per cent conversion for all catalyst concentrations. The general procedure of initial thermal treatment, exposure of sample to field, temperature adjustment in control, and sampling at regular intervals was followed throughout.

Series II: Variation of Temperature and Voltage at Three Catalyst Concentrations and Constant Frequency

A number of experiments at base temperatures of 70° and 100°C. were conducted at 3000 and 4500 v. per cm. The field frequency was 1.55 Mc. The catalyst concentrations and voltages selected were values that could be compared directly with the corresponding data in the previous study at 80°C. The only significant change in procedure was an alteration in the length of time of the prefield thermal treatment. The initial period for these experiments was three hours at 70°C. and half an hour at 100°C.

Series III: Variation of Frequency at Constant Voltage, Catalyst Concentration, and Temperature

The field effect was determined at frequencies of 1.15, 1.55, and 2.39 Mc. at 3000 v., and 1.55, 3.75, 4.47, 6.01, and 7.72 Mc. at 1500 v. per cm. The 3000-v. experiments were not extended beyond 2.39 Mc. owing to the reduced power output of the transmitter at higher frequencies. All these experiments were made at a base temperature of 80°C. and at a catalyst concentration of 1.244 gm. per liter. The experimental methods were the same as those described previously.

Results

The per cent conversion data for a typical experiment are presented in Fig. 4; only that part of the reaction that occurred after the field was applied is shown. Zero time is the time at which the field was applied to the reaction

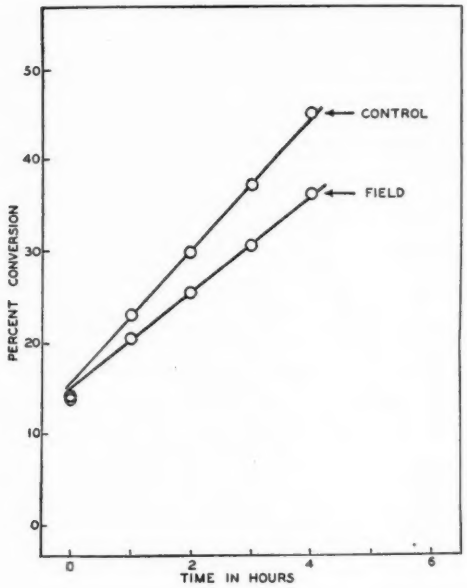

FIG. 4.

cell, i.e., after the initial thermal treatment. In this and in nearly all subsequent experiments the slope of the control rate curve increased after the field was applied, owing to the increased temperature. The slope of the field rate curve was always decreased after the application of the field, and was always less than that of the control in spite of the fact that the steady-state temperatures in the two samples were identical. The reduced slope of the field sample corresponds to an inhibiting effect of the field on the rate of the reaction.

The rate curves for most of the experiments were linear, and reaction rates were calculated directly from the slopes of these lines. Where the rate curves were not linear, reaction rates were calculated from the slopes of tangents drawn to the curves.

Molecular weight data for a typical experiment are presented in Table I. From these data it is apparent that the field had no significant effect on the

TABLE I

MOLECULAR WEIGHT DATA FOR A TYPICAL EXPERIMENT, SHOWING NO EFFECT OF FIELD ON VISCOSITY AVERAGE MOLECULAR WEIGHT

Time, hr.	Molecular weight	
	Field sample	Control sample
0	11200	11400
1	11100	12300
2	11000	11000
3	12000	11400
4	11400	12900

viscosity-average molecular weight of the polymer. Because of the absence of any effect in subsequent experiments, no additional molecular weight data are reported. Possible effects on the molecular weight distribution have not been investigated.

Data for Series I

The data for the experiments to show the effect of the field when catalyst concentration and voltage are varied at constant temperature and frequency are presented in Tables II and III. The per cent conversion data for the first five samples in each experiment are recorded, as well as the time, in hours, of each sampling. The average temperature was the steady-state temperature attained shortly after the field was applied, and was approximately 85.0°C. for all experiments in this series. The temperature coefficient for the catalyzed polymerization of styrene is small, 1.45 (4), and therefore the temperature variations experienced should not invalidate conclusions drawn from the data.

TABLE II

PER CENT CONVERSION DATA FOR EXPERIMENTS AT 3000 V. PER CM. AND 1.55 MC.
Temperature before field applied was 80°C. "Bz_2O_2 conc." in grams benzoyl peroxide per liter of styrene. "Av. temp." is average temperature after field applied.
Time is in hours after field applied

Bz_2O_2 conc.	Av. temp. °C.	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
		Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion
Nil	85.8	0	*2.3 5.1	2	4.6 8.5	3.5	6.5 10.8	5	8.4 13.9	7	10.6 17.0
0.0408	85.8	0	8.5 8.9	1	10.1 10.3	2	11.5 12.6	3	13.0 14.4	4	14.7 17.7
0.156	84.6	0	4.7 4.5	1	7.3 7.6	2	9.4 10.3	3	11.8 12.6	4	14.0 15.3
0.311	83.8	0	 —	2	15.0 15.1	6	24.8 27.7	10	35.3 39.6	14	43.8 48.5
0.622	87.5	0	8.7 8.5	2	15.4 20.1	4	26.0 29.9	6	31.7 37.3	8	39.2 46.3
0.623	85.9	0	8.6 8.9	1	14.0 14.4	2	18.4 19.3	3	22.0 24.2	4	25.7 28.4
0.723	86.5	0	10.3 9.5	2	18.9 21.7	4	29.8 31.8	6	35.2 37.6	8	43.4 47.3
0.934	84.3	0	11.9 13.1	2	22.0 25.2	4	32.0 37.2	6	40.6 48.0	8	52.6 61.3
0.934	83.7	0	12.9 13.0	2	22.5 25.7	4	31.6 35.6	6	39.2 47.6	8	49.5 61.9
1.244	86.7	0	13.3 12.2	2	25.1 29.0	4	36.8 44.4	6	50.0 63.4	—	—
1.554	86.8	0	16.3 14.8	1	22.2 23.9	2	29.2 31.2	3	35.0 39.5	4	41.6 48.0
1.866	84.5	0	16.6 16.9	2	32.7 36.7	4	48.8 53.6	6	65.0 77.1	—	—
2.182	85.6	0	16.6 19.2	1	23.9 25.7	2	32.5 35.2	3	40.4 45.1	4	48.5 55.2

** For each experiment the first line shows the results obtained with the field sample, and the second line those with the control sample.*

TABLE III

PER CENT CONVERSION DATA FOR EXPERIMENTS AT 4500 AND 1500 V. PER CM. AND 1.55 MC. Temperature before field applied was 80°C.

Bz_2O_2 conc.	Av. temp. °C.	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
		Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion
4500 volts											
Nil	87.1	0	*15.2 14.1	2	16.7 17.4	4	18.6 21.2	6	21.9 25.6	7.5	24.8 29.8
0.0408	86.5	0	5.5 6.4	1	7.3 8.6	2	8.7 11.3	3	10.1 13.2	4	11.6 16.6
0.156	84.2	0	5.0 5.2	1	8.0 8.9	2	10.8 11.6	3	13.2 15.4	4	15.6 17.5
0.723	85.9	0	9.2 8.9	2	15.8 20.6	3	20.5 25.6	4	22.4 31.0	6	30.7 43.2
1.244	86.0	0	14.2 13.8	1	20.4 23.0	2	25.3 29.9	3	30.7 37.3	4	36.3 45.3
1.554	87.0	0	15.7 14.6	2	25.4 30.4	3	29.0 37.8	4	33.5 45.5	5	40.5 58.2
1.866	85.2	0	17.3 17.1	1	25.4 26.4	2	31.0 37.3	3	37.5 46.4	4	46.5 58.6
2.182	86.9	0	17.8 18.3	1	25.0 30.5	2	29.8 39.2	3	35.7 44.8	4	39.2 63.0
2.182	85.6	0	17.5	1	26.1 30.1	2	32.2 42.2	3	40.7 54.3	4	47.0 67.9
2.600	83.8	0	21.5 21.7	1	27.1 31.3	2	34.7 42.2	3	43.5 53.7	4	52.9 69.8
1500 volts											
0.723	84.9	0	10.7 10.5	2	21.6 22.4	3	25.6 26.4	4	29.6 31.0	6	37.8 39.0
1.244	85.4	0	13.0 13.0	2	25.8 29.1	3	33.6	4	39.2 42.1	5	46.9 48.7
2.182	85.0	0	18.2 18.3	1	25.6 25.9	2	34.4 35.3	3	42.2 43.3	4	51.1 51.7

** For each experiment the first line shows the results obtained with the field sample, and the second line those with the control sample.*

Reaction rates calculated from the slopes of the rate curves for both the control (k_C) and field samples (k_F) for the 3000- and 4500-v. data are plotted against the square root of the catalyst concentration in Fig. 5. For normal polymerizations a linear relation has been shown to exist between the rate of catalyzed styrene polymerization and the square root of the catalyst concentration (1). The 1500-v. data are not shown in Fig. 5 since only three points were obtained. The upper curve, for the control experiments, is linear over most of the catalyst range covered. The change in slope apparent at low benzoyl peroxide concentrations may be due to an acceleration of the rate by styrene peroxides formed by atmospheric oxygen. The reaction rate curves for the field samples show a distinct curvature. The data for the 4500-v. experiments are somewhat scattered, but the most representative curve was drawn through the points.

The effect of the field on the rate of polymerization at various catalyst concentrations is best illustrated by a plot of ratios of control and field rates against the square root of the catalyst concentration. These data are presented in Fig. 6. Values of k_C and k_F for various catalyst concentrations were taken

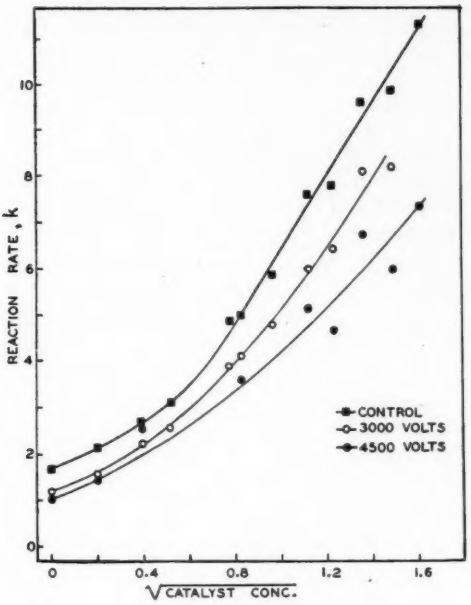
REACTION RATE, k
0
2
4
6
8
10
0
0.4
0.8
1.2
1.6
√CATALYST CONC.
CONTROL
3000 VOLTS
4500 VOLTS

FIG. 5.

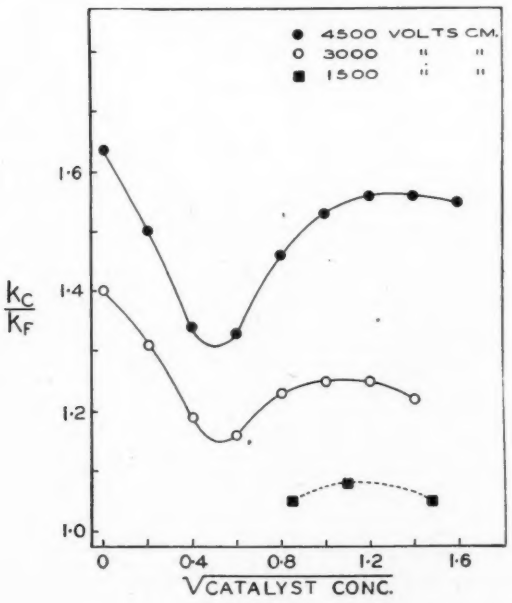
4500 VOLTS CM.
3000 " "
1500 " "
$\frac{k_C}{k_F}$
1·0
1·2
1·4
1·6
0
0·4
0·8
1·2
1·6
√CATALYST CONC.

FIG. 6.

from the smooth curves in Fig. 5 for the 3000-and 4500-v. experiments. Also shown are the ratios for the three experiments at 1500 v. Owing to the uncertainty resulting from the lack of data, a dotted line is drawn through these latter points.

Using k_C and k_F values taken from the curves in Fig. 5 and the experimental values for the 1500-v. data the per cent reduction in rate resulting from the three voltages at each of three catalyst concentrations was calculated. These results are shown in Table IV. The data show that the inhibition increases as the 1.8th power of the voltage. An extrapolation of these results to 100% reduction in rate indicates that a field of approximately 9000 v. per cm. at

TABLE IV

DATA SHOWING PER CENT REDUCTION IN RATE AT EACH OF THREE VOLTAGES AT 1.55 MC.

Catalyst conc.	Av. temp. °C.	Volts per cm.	k_C	k_F	Per cent red'n. in rate $\frac{k_C - k_F}{k_C} \times 100$	Av. per cent red'n. in rate
0.723	84.7	1500	4.27	4.07	4.7	5
1.244	85.4		7.15	6.65	5.6	
2.182	85.0		8.40	8.00	4.8	
0.723	85.4	3000	5.05	4.12	18.4	18
1.244	85.4		7.37	5.93	19.5	
2.182	85.4		10.30	8.63	16.2	
0.723	85.4	4500	5.05	3.47	31.7	34
1.244	85.4		7.37	4.76	35.4	
2.182	85.4		10.30	6.70	34.6	

TABLE V

PER CENT CONVERSION DATA FOR EXPERIMENTS AT 4500 AND 3000 V. PER CM.
Temperature before field applied was 70°C.

BzO_2 conc.	Av. temp. °C.	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
		Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion
3000 volts											
0.723	72.1	0	* 6.7 7.0	1	9.1 9.9	2	11.7 12.3	3	14.2 15.0	—	—
1.244	72.6	0	9.0 10.2	1	12.9 13.6	2	14.8 17.4	3	16.8 19.6	4	19.8 23.3
1.866	72.6	0	11.0 10.9	1	14.9 15.4	2	18.4 18.3	3	21.3 23.4	4	24.7 26.4
4500 volts											
0.723	75.3	0	6.4 6.3	1	9.4 10.4	2	11.6 13.2	3	13.9 15.9	4	17.5 19.3
1.244	74.5	0	9.0 8.6	1	12.5 13.0	2	15.6 16.6	3	18.9 19.9	4	21.6 22.5
1.866	73.6	0	11.0 10.4	2	17.5 21.1	3	21.4 24.8	4	24.0 28.2	5	27.2 32.4

* *For each experiment the first line shows the results obtained with the field sample, and the second line those with the control sample.*

1.55 Mc. and 80°C. would completely inhibit the catalyzed polymerization of styrene. It is possible, however, that some additional factor might invalidate this extrapolation.

Data for Series II

The data for the experiments at 70°C. at two voltages and three catalyst concentrations are presented in Table V. The rate curves for the experiments at 70° and 80°C. were linear, and reaction rates were calculated as before by measuring the slopes of these straight lines. The reaction rates (k_C and k_F) and ratios of k_C to k_F for these experiments are presented in Table VI. The retardation for the 3000-v. experiments was approximately the same for the 70° and 80°C. data. At 4500 v. per cm. the retardation in rate was greater at 80° than it was at 70°C.

TABLE VI

RATE CONSTANTS FOR EXPERIMENTS AT 70°C.; 1.55 MC.

Catalyst conc.	Av. temp., °C.	k_C	k_F	k_C/k_F
3000 volts				
0.723	72.1	2.70	2.45	1.10
1.244	72.6	3.13	2.57	1.22
1.866	72.6	3.87	3.33	1.16
4500 volts				
0.723	75.3	3.03	2.63	1.15
1.244	74.6	3.50	3.13	1.12
1.866	75.4	3.89	3.23	1.21

At 100°C., the rate curves were distinctly curved. This was attributed to the rapid disappearance of the catalyst from the reaction mixture, since benzoyl peroxide has a temperature coefficient for dissociation of approximately 4.5 (12). Attempts were made to obtain initial rates from tangents drawn to the curves, but the results were not satisfactory, and hence the data for the experiments at 100°C. are not reported. Qualitatively it was found that the field effect still existed at this temperature, and that the relation between field effect and voltage gradient more closely paralleled the 80° than the 70°C. data.

From the reaction rate data at 70° and 80°C. approximate temperature coefficients and activation energies for both field and control samples were calculated for this temperature range. Although the results must be considered as qualitative only owing to the few data upon which they are based, fields of 4500 v. per cm. appeared to cause a reduction in the activation energy for the catalyzed polymerization of styrene of approximately 50%. Only a slight eduction in activation energy was observed at 3000 v.

Data for Series III

The data for the experiments with varying frequency at constant voltage, catalyst concentration, and temperature are presented in Table VII. Neither the per cent conversion nor the molecular weight of the polymer was significantly affected by the variation in frequency investigated at 3000 and 1500 v. per cm.

TABLE VII

PER CENT CONVERSION DATA FOR FREQUENCY STUDY
Temperature before field applied was 80°C. Benzoyl peroxide concentration was 1.244 gm. per liter of styrene

Freq., Mc.	Av. temp., °C.	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
		Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion	Time, hr.	Per cent conversion
3000 volts											
1.15	83.4	0	*14.7 14.6	1	20.4 22.4	2	27.0 30.4	3	32.3 36.9	4	38.7 45.7
1.55	86.7	0	13.3 12.2	2	25.1 29.0	4	36.8 44.4	6	50.0 63.4	—	—
2.39	83.3	0	14.4 14.4	1	21.4 22.4	2	27.4 29.3	3	32.7 35.2	4	39.4 44.6
1500 volts											
1.55	85.4	0	13.0 13.0	2	25.8 29.1	3	33.6	4	39.2 42.1	5	46.9 48.7
3.75	83.8	0	15.3 14.4	1	22.3 22.1	2	27.6 28.5	3.25 2.75	36.0 34.7	4	40.1 44.3
4.47	83.8	0	14.2 14.2	1	21.1 22.1	2	27.6 29.9	3	33.7 37.3	4	40.3 45.4
6.01	83.8	0	13.6 15.0	1	22.2 23.9	2	28.6 30.8	3	35.5 38.8	4	42.0 45.1
7.72	84.5	0	14.2 14.0	1	21.1 22.6	2	26.9 29.6	3	33.5 37.0	4	41.7 47.9

** For each experiment the first line shows the results obtained with the field sample, and the second line those with the control sample.*

Discussion

The main objective of this study was to determine whether, with careful control of temperature conditions, any effect of a high frequency electrical field on the rate of a chemical reaction might be demonstrated. There seems no reason to doubt that the observed retardation in rate of polymerization of styrene represents a genuine effect of the applied field. This retardation might be due to an effect of the field on the polymerization itself, or it might reflect a decreased rate of dissociation of the catalyst, benzoyl peroxide, into reaction-initiating fragments, in the presence of the field. Experiments are now in progress to determine whether the rate of decomposition of benzoyl peroxide in solution is altered by such fields, and, if so, whether the behavior of the styrene polymerization reaction can be satisfactorily accounted for on this basis.

Acknowledgments

Grateful acknowledgment is made to Dr. J. S. Howes and Mr. L. Geddes of the Department of Electrical Engineering, McGill University, for advice on construction of some of the radio equipment used, and to the Committee on Research, McGill University, for financial assistance in the publication of this manuscript.

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THE INFRARED SPECTRA OF TRICHLOROETHYLENE ($CHCl = CCl_2$ AND $CDCl = CCl_2$) AND ASYMMETRICAL TETRACHLOROETHANE ($CH_2Cl–CCl_3$ AND $CD_2Cl–CCl_3$) FROM 2.5μ TO 25μ[1]

By H. J. Bernstein

Abstract

The infrared spectra of light and heavy trichloroethylene and asymmetrical tetrachloroethane have been obtained from 2.5 to 25μ. Tentative assignments of the fundamentals have been made.

The deuterated compounds were prepared in the following manner:

(1) $CaC_2 + D_2O = C_2D_2 + CaO$

(2) $C_2D_2 + 2Cl_2 = C_2D_2Cl_4$

(3) $2C_2D_2Cl_4 + Ca(OD)_2 = 2CDCl = CCl_2 + CaCl_2 + 2D_2O$

(4) $CDCl = CCl_2 + DCl \xrightarrow{AlCl_3} CD_2Cl - CCl_3$

The heavy trichloroethylene contained about 5% of the light compound whereas the heavy tetrachloroethane was practically pure (see spectra). The spectra were obtained by Dr. J. Powling* in the gas and liquid phases with a Perkin–Elmer spectrometer (Model 12C) used in conjunction with a Brown recorder; they are shown in Figs. 1, 2, 3, and 4.

Table I lists the observed infrared and Raman spectra of light trichloroethylene and the infrared spectrum of heavy trichloroethylene. The last column gives a reasonable assignment where the frequencies correspond to the modes of vibration shown schematically in Fig. 5.

Since trichloroethylene has a plane of symmetry there are two types of vibration, the symmetrical with nine modes and the antisymmetrical with three modes—all active in both Raman and infrared.

Using the dimensions of the molecule obtained from electron diffraction (2) to obtain the principal moments of inertia the isotopic product rule ratios (1) are calculated as 1.97 and 1.38 for the symmetrical and the antisymmetrical types respectively. The ratios calculated from the frequencies observed in the liquid are 1.97 and 1.33 respectively if the low lying fundamentals are assumed to change very little on deuterium substitution.

The assignment therefore is consistent with the product rule.

[1] *Manuscript received September 13, 1949.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 2104.
**National Research Laboratories Postdoctorate Fellow, 1949-1950.*

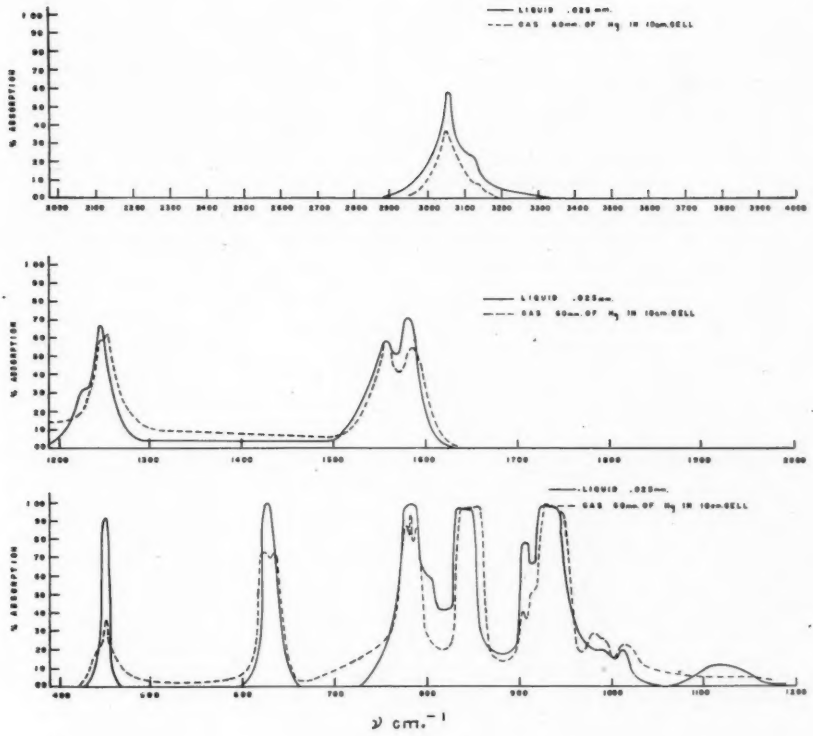

FIG. 1. *Infrared spectrum of* $CCl_2=CHCl$.

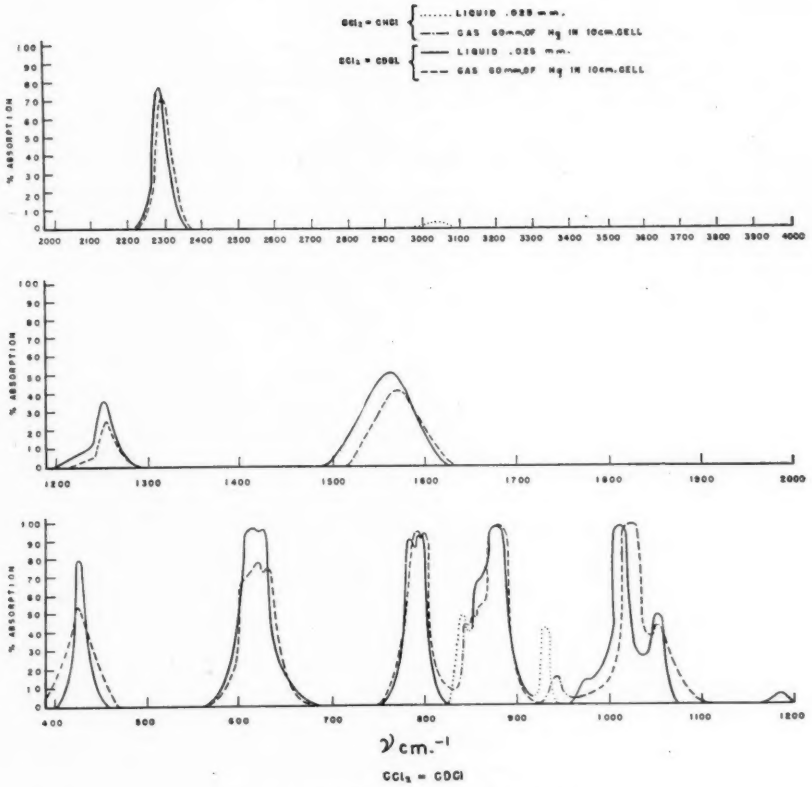

FIG. 2. *Infrared spectrum of* $CCl_2=CDCl$.

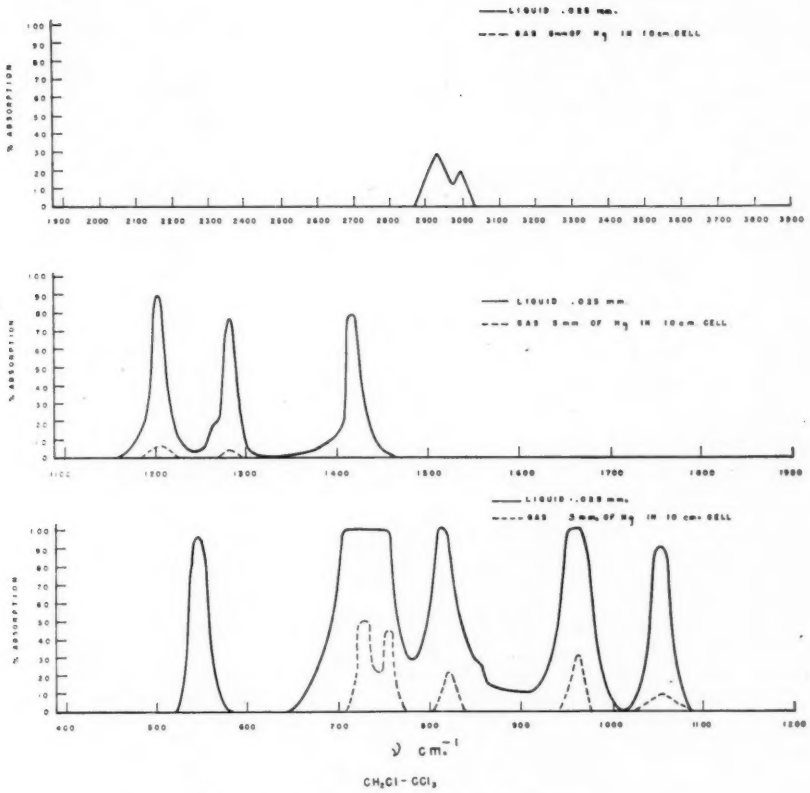
LIQUID .035 mm.
GAS 5 mm OF Hg IN 10 cm CELL
% ABSORPTION
LIQUID .035 mm.
GAS 5 mm OF Hg IN 10 cm CELL
% ABSORPTION
LIQUID .035 mm.
GAS 5 mm OF Hg IN 10 cm CELL
% ABSORPTION
ν cm⁻¹
CH2Cl - CCl3

FIG. 3. *Infrared spectrum of* CH_2Cl–CCl_3.

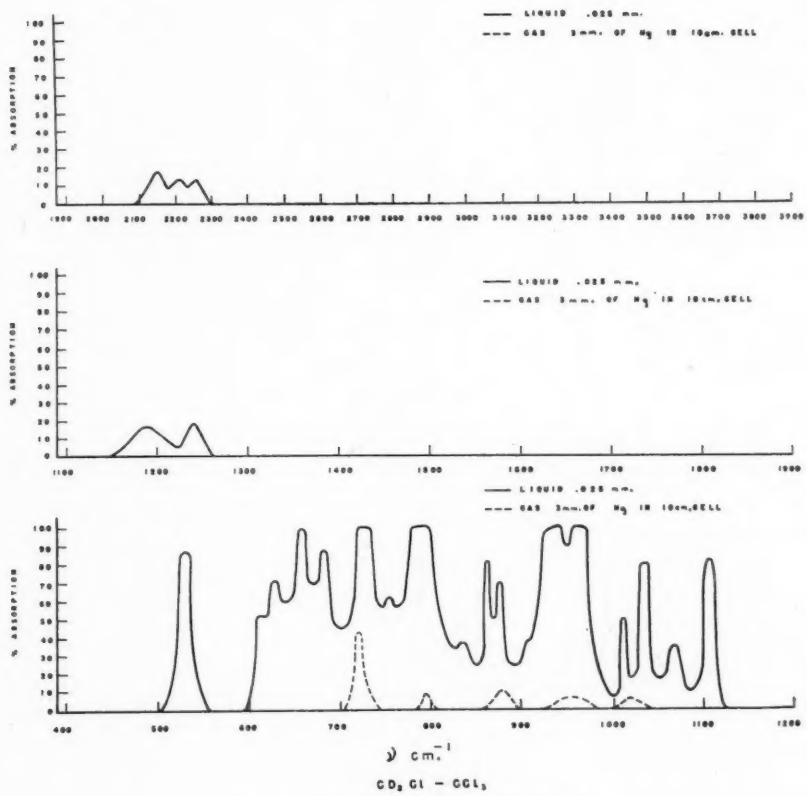

FIG. 4. *Infrared spectrum of* CD_2Cl–CCl_3.

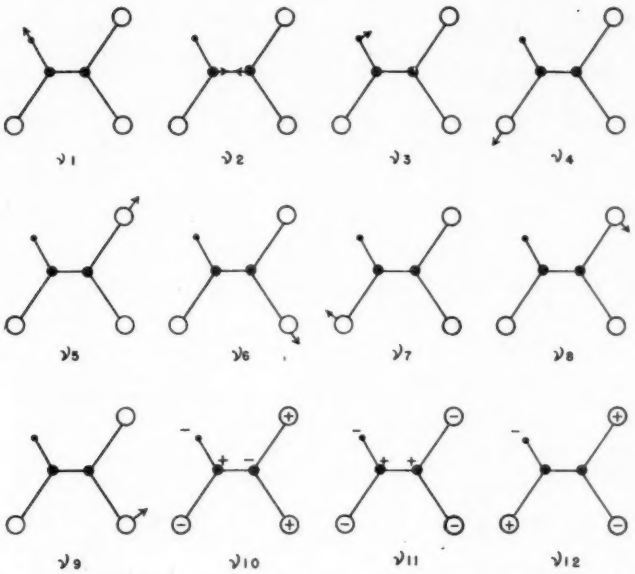

FIG. 5. *Modes of vibration of the trichloroethylene molecule* • = *H*, ● = *C*, ○ = *Cl*.

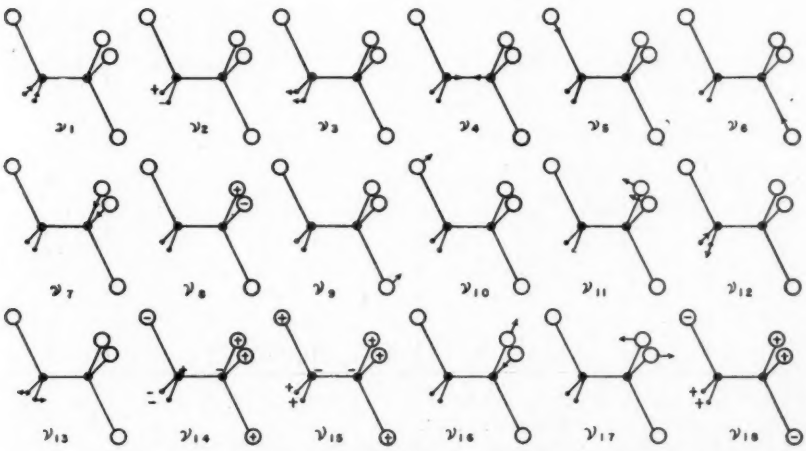

FIG. 6. *Modes of vibration of the tetrachloroethane molecule* • = *H*, ● = *C*, ○ = *Cl*.

Table II lists the observed infrared and Raman spectra of light tetrachloroethane and the infrared spectrum of heavy tetrachloroethane. The last column gives a reasonable assignment where the frequencies correspond to the modes depicted schematically in Fig. 6.

Since tetrachloroethane has a plane of symmetry there are 11 symmetric type vibrations and 7 antisymmetric, all active in Raman and infrared. The product rule ratios are about $2^{3/2}$ for both types since the moments of inertia and molecular weight change very little on substitution of 2D for 2H. The ratios calculated from the observed frequencies (assuming the low frequencies in the heavy tetrachloroethane to be the same as in the light) are consistent with these values and indicate that the assignment is reasonable.

Acknowledgment

Thanks are due to Mr. L. C. Leitch for supplying the samples of light and heavy trichloroethylene and tetrachloroethane, and to Miss E. Miller for reduction of the spectra.

TABLE I

$CHCl=CCl_2$					$CDCl=CCl_2$		
Raman* liquid	Raman† liquid	I. R.† gas	I. R. liquid (this work)	I. R. gas (this work)	I. R. liquid (this work)	I. R. gas (this work)	Assignment
3080(4*b*)	3082*s*	3096*m PQR*	3080*s*	3079*s*	2274*s*	2290*s*	ν_1
1585(6)	1586*s*	1590*m*	1585*s*	1590*s*	1560*s*	1565*s*	ν_2
			1555*w*	1555*m*	1250*w***	1252*w*	$2\nu_{11}$
	1385*s*						?
					1184*vvw*		$\nu_3+\nu_9$
1248(2*b*)	1242*s*	1250*m PQR*	1248*s*	1250*s*	1013*s*	1020*s*	ν_3
	1226*w*		1230*m*		1049*m*	1049*w*	$\nu_6+\nu_{11}$
			1112*w*				$\nu_4+\nu_8$
			1013*w*	1015*w*			$\nu_5+\nu_7$
				985*w*			$\nu_{11}+\nu_{12}$
933(1)	947*w*	940*s PR*	933*s*	933*s*	875*s*	875*s*	ν_{10}
			907*m*	904*w*	856*m*		$2\nu_6$
	845*w*	850*s PQR*	842*s*	850*s*	796*s*	800*s*	ν_4
			805*w*		783*s*§		$\nu_5+\nu_9$
775(2)	786*m*	784*s PQR*	783*s*	783*s*	625*s*‡	627*s*	ν_{11}
	765*w*						$2\nu_7$
628(5)	628*s*	633*s PQR*	630*s*	630*s*	615*s*	616*s*	ν_5
452(3)	449*m*		452*s*	452*s*	425*s*	424*s*	ν_6
380(5)	381*s*						ν_7
274(5)	274*s*						ν_8
211(4)	212*s*						ν_{12}
172(5)	165*s*						ν_9

* *A. Dadieu and K. W. F. Kohlrausch. Monatsh., 55:58. 1930.*

† *Ta-You Wu. Phys. Rev. 46:465. 1934.*

‡ *Estimated at 625 because it is overlapped by the strong band at 610 to 630 cm.*$^{-1}$

§ *Resonance with 796 enhances the intensity of this band.*

** *Some of the intensity of this band is due to the light $CHCl=CCl_2$ as impurity.*

TABLE II

CH_2Cl–CCl_3			CD_2Cl–CCl_3		
Raman* liquid	I. R. liquid	I. R. gas	I. R. liquid	I. R. gas	Assignment
3017(8)	3000*s*		2255*s*		ν_{12}
2961(9)	2980*s*		2210*s*		ν_1
			2150*m*		$2\nu_3$
			1280*w*		$\nu_7+\nu_{14}$
			1240*w*		$\nu_7+\nu_{15}$
			1185*w*		$\nu_1+\nu_{16}$
1281(4)	1280*s*	1280	1105*s*		ν_3
			1070*w*		$\nu_{16}+\nu_8$
1420(6)	1415*s*		1040*s*		ν_2
			1010*m*	1015	$\nu_{16}+\nu_9$
1202(4)	1200*s*	1205	958*s*	960	ν_{13}
958(3)	958*s*	960	940*s*		ν_4
			905*w*		$\nu_6+\nu_{11}$
	895*w*		875*m*	880	$\nu_7+\nu_8$
			860*m*		$\nu_7+\nu_9$
			830*w*		$\nu_7+\nu_{10}$
1056(5)	1050*s*	1060	790*s*	793	ν_{14}
			752*w*		$\nu_7+\nu_{11}$
813(9*b*)	810*s*	818	730*s*	725	ν_{15}
765(2)		750*s*	685*s*		ν_{16}
747(3)	700–750*s*	730*s*	675†		ν_5
718(6*b*)			660*s*		ν_6
			620*m*		$\nu_{18}+\nu_7$
549(10)	525*s*		515*s*		ν_7
381(9)					ν_8
336(7)					ν_9
308(7)					ν_{10}
242(8)					ν_{11}
157(5)					ν_{17}
118(5*b*)					ν_{18}

* *S. Mizushima, Y. Morino, M. Kawano, and R. Otiai. Sci. Papers Inst. Phys. Chem. Research. 42, Jan. 1, 1944.*

† *Overlapped by strong band at 685 cm.*$^{-1}$

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THE *CIS–TRANS* ISOMERIZATION OF AZOBENZENE IN SOLUTION[1]

BY J. HALPERN,[2] G. W. BRADY,[3] AND C. A. WINKLER

Abstract

Relations for the solvent effect on the rate of a unimolecular, nonionic reaction are derived, using existing theories of solutions and of chemical kinetics. The kinetics of the *cis–trans* isomerization of azobenzene were investigated in 16 pure solvents. A linear relation between the activation energy, E, and the square root of the internal pressure of the solvent, $(P'_S)^{1/2}$ was found, in agreement with the theory. Linear relations between log A and E, and between log k and $(P'_S)^{1/2}$ were also found, but the results for the reaction in highly polar solvents deviated significantly from these relations. The kinetics of the reaction in mixed solvents indicate that the azobenzene is preferentially surrounded by the component in which it is more readily soluble.

Introduction

The majority of reactions which occur in solution, and of which the kinetics have been investigated from the point of view of the solvent effect, are bimolecular and involve reactants which are either ions or highly polar molecules (19). Quantitative application of theories of solvent effect has also been limited almost entirely to these types of reactions (7, 16). There remains therefore considerable need for further study in the field of solution kinetics, particularly of unimolecular and nonionic reactions. The present paper describes an attempt which has been made to extend to this type of system both the theoretical treatment and experimental investigation of the effect of the solvent on reaction rates.

The Kinetics of Reactions in Solution

It has long been customary to express the rates of chemical reactions by means of the well known Arrhenius equation,

$$k = Ae^{-E/RT}, \tag{1}$$

where k is the specific rate constant of the reaction,
E is the activation energy,
R is the molar gas constant,
T is the absolute temperature,
and A is the frequency factor of the reaction.

The effect of changing the solvent on the rate of a reaction is generally reflected in variations in both A and E. It has been almost impossible to

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Contribution from the Physical Chemical Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.
[2] *Holder of a Fellowship under the National Research Council of Canada. Present address: Department of Chemistry, University of Manchester.*
[3] *Holder of a Fellowship under the National Research Council of Canada. Present address: Jones Chemical Laboratory, University of Chicago.*

account theoretically for these variations in terms of the classical collision theory of reaction rates, since these quantities, particularly A, have been regarded as semiempirical constants, of which the theoretical significance was at best qualitatively understood.

A somewhat more satisfactory approach to the treatment of reaction rates has been provided by the Transition State Theory, first enunciated by Eyring and his coworkers (27). This theory allows the rate of a reaction to be expressed in terms of the thermodynamic properties of the reacting system. Thus, the rate constant, k, of the simple unimolecular reaction,

$$X \longrightarrow M^* \longrightarrow Y$$

is given by the following expression,

$$k = \kappa \left(\frac{kT}{h}\right) e^{\Delta S^*/R} \quad e^{-\Delta H^*/RT}, \tag{2}$$

where k is the Boltzmann constant,
T is the absolute temperature,
and h is the Planck constant.
ΔS^* is the entropy of activation, defined by,

$$\Delta S^* = S_{M^*} - S_X, \tag{3}$$

where S_{M^*} is the molar entropy of M^*,
and S_X is the molar entropy of X.
ΔH^* is the heat of activation and is similarly defined,
κ is called the transmission coefficient and represents the probability that the activated complex will react to give a molecule of product rather than return to the initial state. For many reactions, $\kappa = 1$.

By a comparison of Equations (1) and (2), it can be shown (7) that for a reaction in solution,

$$E = \Delta H^* + RT \tag{4}$$

and

$$A = e\kappa \left(\frac{kT}{h}\right) e^{\Delta S^*/R}. \tag{5}$$

The frequency factor of the reaction is thus seen to be related to the entropy of activation.

For a reaction in solution, the thermodynamic functions, H and S, can be replaced by the corresponding partial molal quantities, $\bar{H}$ and $\bar{S}$, leading to the following relations.

$$\begin{aligned} \Delta H^* &= \bar{H}_{M^*} - \bar{H}_X \\ &= (H^0_{M^*} + \Delta\bar{H}_{M^*}) - (H^0_X + \Delta\bar{H}_X) \\ &= \Delta H^*_0 + (\Delta\bar{H}_{M^*} - \Delta\bar{H}_X) \end{aligned} \tag{6}$$

where $H^0_{M^*}$ and H^0_X are the heat contents of M^* and X respectively in their standard states, taken for convenience as being the pure liquids,

and $\Delta\bar{H}_{M^*}$ and $\Delta\bar{H}_X$ are their partial molal heats of solution.
ΔH_0^* represents the activation energy of the reaction when X and M^* are in their standard states.

The entropy of activation of a reaction in solution may be similarly expressed.

$$\Delta S^* = \Delta S_0^* + (\Delta\bar{S}_{M^*} - \Delta\bar{S}_X), \tag{7}$$

where all the symbols are analogously defined.

The rate of a reaction in solution can also be expressed (16) in terms of the activity coefficients of the reactant and activated complex,

$$k = k_0 \frac{\gamma_X}{\gamma_{M^*}}, \tag{8}$$

where k_0 is the standard state rate of the reaction,
γ_X is the activity coefficient of the reactant,
and γ_{M^*} is the activity coefficient of the activated complex.

The effect of the solvent on the rate of a reaction is thus seen to be entirely related to the heats and entropies of solution, or alternatively to the activity coefficients, of the reactant and the activated complex, and the calculation of the solvent effect reduces to the purely thermodynamic problem of estimating these quantities.

This has been done by Scatchard (23) and Kirkwood (14) for systems where the reactants are either ions or highly polar molecules. The relations so derived are in agreement with the observed solvent effects in these types of systems (7, 16).

It is with reactions involving ordinary molecules, i.e., those in which the intermolecular forces are predominantly nonpolar, that the least progress has been made toward a quantitative understanding of the solvent effect. This is due largely to the difficulty involved in estimating the magnitudes of $\Delta\bar{H}$ and $\Delta\bar{S}$ for these molecules.

An approximate treatment of such systems has been developed by Hildebrand (12, 13), using the concept of the regular solution. A regular solution is defined as one in which the distribution and orientation of molecules is completely random. The entropy of solution is therefore assumed to have the same value as for an ideal solution of similar composition, i.e.,

$$\bar{S}_r - \bar{S}_i = 0$$

and $$\bar{F}_r - \bar{F}_i = \bar{H}_r - H^0,$$

where $\bar{S}_r$, $\bar{F}_r$, and $\bar{H}_r$ are the partial molal entropies, free energy, and heat content of a component in a regular solution,
$\bar{S}_i$ and $\bar{F}_i$ are the corresponding partial molal quantities in an ideal solution of similar composition,
and H^0 is the heat content of the same component in its pure liquid state.

Although this condition is rarely fulfilled it is likely that it is approached in solutions where the intermolecular forces are predominantly nonpolar.

However, while the errors in $\Delta\bar{S}$ and $\Delta\bar{F}$, introduced by considering a real solution to be regular, may be significant, Kirkwood (15) has shown that the error in $\Delta\bar{H}$ is generally quite small. It is therefore convenient to use the concept of a regular solution to derive a relation for the effect of the solvent on the activation energy only of the reaction. Such a relation should be applicable to all systems in which the intermolecular forces are predominantly nonpolar. London (18) has shown that this is the case even with fairly polar molecules, such as hydrogen chloride, where large orientation effects might be expected. Only for ions or very highly polar molecules, such as water, do the polar forces predominate.

Hildebrand (12, 13) has shown that for a dilute regular solution of X_1 in X_2, the partial molal heat of solution of X_1 is given by the expression,

$$\Delta\bar{H}_1 = V_1[(P_1')^{1/2} - (P_2')^{1/2}]^2,$$

where V_1 is the molar volume of X_1
and P_1' and P_2' are the internal pressures of X_1 and X_2 respectively.
Applying this to the unimolecular reactions previously discussed, the heat of solution of the reactant X is given by

$$\Delta\bar{H}_X = V_X[(P_X')^{1/2} - (P_S')^{1/2}]^2,$$

where V_X is the molar volume,
P_X' the internal pressure of the reactant,
and P_S' is the internal pressure of the solvent.
The heat of solution of the activated complex, M^*, is given by a similar expression,

$$\Delta\bar{H}_{M^*} = V_{M^*}[(P_{M^*}')^{1/2} - (P_S')^{1/2}]^2.$$

Combining these equations with Equation (6) and assuming that V_X and V_{M^*} are equal, leads to the following relation,

$$\Delta H^* = \Delta H_0^* + V_X[\{(P_{M^*}')^{1/2} - (P_S')^{1/2}\}^2 - \{(P_X')^{1/2} - (P_S')^{1/2}\}^2].$$

On expansion this becomes,

$$\Delta H^* = \Delta H_0^* + V_X[\{(P_X')^{1/2} - (P_{M^*}')^{1/2}\}2(P_S')^{1/2} - (P_X' - P_{M^*}')] = E - RT. \quad (9)$$

Since P_{M^*}' and P_X' are constants for a given reaction, this corresponds to a linear relation between ΔH^* or E and $(P_S')^{1/2}$.

Eyring (16) has derived a relation for the effect of the solvent on the rate of a reaction, in terms of the free energies of solution of the reactant and activated complex. Using the fact that in a regular solution,

$$\bar{F}_r - \bar{F}_i = \bar{H}_r - H^0,$$

it can be shown that this relation becomes equivalent to Equation (9) for a regular solution.

To derive an expression for the solvent effect on the frequency factor, use may be made of a semiempirical relation first established by Evans and Polanyi (4). They found that when a given solute is dissolved in a series of different

solvents, the heats and entropies of solution are often related by an expression of the form,

$$\frac{\Delta\bar{S}}{R} = \rho\Delta\bar{H} + C, \tag{10}$$

where $\Delta\bar{S}$ is the partial molal entropy of solution,
$\Delta\bar{H}$ is the partial molal heat of solution
and ρ and C are constants for a given solute.

Expressions of this form may be substituted for $\Delta\bar{S}_{M^*}$ and $\Delta\bar{S}_X$ in Equation (7), giving

$$\frac{\Delta S^*}{R} = \frac{\Delta S_0^*}{R} + (\rho_{M^*}\Delta\bar{H}_{M^*} - \rho_X\Delta\bar{H}_X) + (C_{M^*} - C_X).$$

Since the values of ρ do not vary greatly for different solutions, ρ_{M^*} and ρ_X may be assumed to be equal. This expression then simplifies to

$$\frac{\Delta S^*}{R} = \left(\frac{\Delta S_0^*}{R} - \rho_X\Delta H_0^* + \Delta C^*\right) + \rho_X\Delta H^*,$$

where $\Delta C^* = C_{M^*} - C_X$.

When this is combined with Equation (5), a linear relation between log A and E or ΔH^* for the reaction in different solvents, is obtained,

$$\log A = \log\left(e\kappa\frac{kT}{h}\right) + \frac{1}{2.303}\left(\frac{\Delta S_0^*}{R} - \rho_X\Delta H_0^* + \Delta C^*\right) + \frac{\rho_X}{2.303}\Delta H^* \tag{11}$$

This type of relation has often been observed with reactions in solution. It has been derived by Evans and Polanyi (4) in a manner similar to that used above. It has also been interpreted kinetically by Fairclough and Hinshelwood (5) and by Waring and Becher (24) from the point of view of the collision theory. Ogg and Rice (20) have arrived at a similar relation from a consideration of the effects of solvation.

The combination of Equations (1), (9), and (11) leads to a linear relation between log k and $(P_S')^{1/2}$ for the reaction in different solvents, of the form,

$$\log k = J + L(P_S')^{1/2}, \tag{12}$$

where J and L are functions of T only for a given reaction.

It should be pointed out that Equation (9), expressing the effect of the solvent on the activation energy, was derived by considering the solution as being regular. However, in deriving Equation (11), this restriction was dropped and an attempt was made to estimate the entropy of solution, using the empirical properties of real solutions.

To test the validity of these considerations, a study was made of the solvent effect on the kinetics of the *cis–trans* isomerization of azobenzene. This reaction, first investigated by Hartley (9, 10), was chosen because it is unimolecular, and involves molecules which are not too highly polar. Consequently the treatment outlined above should be applicable to it.

Hartley (9) first reported the isolation of two forms of azobenzene corresponding to *cis* and *trans* isomers. Azobenzene normally occurs in the *trans* form which is considerably more stable than the *cis*. When a solution of *trans*-azobenzene is irradiated with ultraviolet light it is partially converted to the *cis* isomer which may then be separated chromatographically (1) or by fractional crystallization (10). The crystal structures of the two isomers have been examined by X-ray diffraction methods (8, 22). The results confirm the alleged structures of the two forms and indicate that the instability of the *cis* isomer is due to the repulsion or steric hindrance of the two benzene ring substituents (21).

While the solid form of *cis*-azobenzene is fairly stable in the absence of light, in solution it is converted completely to the *trans* isomer. This reaction proceeds at measurable rates between room temperature and about 100°C. Hartley (10) has studied its kinetics in a number of solvents and reported that while the rate varied considerably in different solvents there was no appreciable variation in the activation energy which was about 23,000 cal. per mole. The reaction is catalyzed by H^+ ions.

Experimental Methods

Preparation of cis-Azobenzene

Commercial azobenzene consists almost entirely of the *trans* isomer. It was supplied by Brickman and Co., Montreal, and had a melting point of 67°C. The procedure followed in converting it to the *cis* isomer and separating the latter was essentially that of Hartley (10). One hundred grams of azobenzene was dissolved in a liter of glacial acetic acid containing 20 ml. of water. The solution was irradiated with a G.E. (275 W) Sunlamp for 24 hr. during which time an appreciable darkening in the color was observed. It was subsequently diluted in the dark with 900 ml. of water (this had the effect of precipitating nearly all of the *trans* and none of the *cis* isomer) and filtered. The residue was redissolved and subjected to further exposure, as described above. The filtrate was further diluted with a liter of water and extracted with chloroform. The chloroform was evaporated from the extract in a vacuum desiccator, and the crude product thus obtained was recrystallized from petroleum ether, until a constant melting point of 70°C. was obtained. The yield of pure *cis* isomer, obtained from three exposures, was about 10 gm. All operations involving *cis*-azobenzene were performed in the dark, as the two isomers are photochemically interconverted.

Analytical Procedures

Solutions were analyzed for both isomers photometrically, using a Beckmann Spectrophotometer. It was found, in agreement with the results of Cook (2), that while both isomers show maxima in their absorption spectra at about 4400Å, the *cis* form has a considerably higher absorption in this region. This enabled the composition of solutions of known total concentration to be deter-

mined by measuring the optical density, and referring to calibration graphs such as those shown in Fig. 1. Since the absorption varied slightly with the solvent, calibration graphs were constructed for each of the solvents used. The linearity of the graphs indicates that Beer's law is obeyed throughout the range considered.

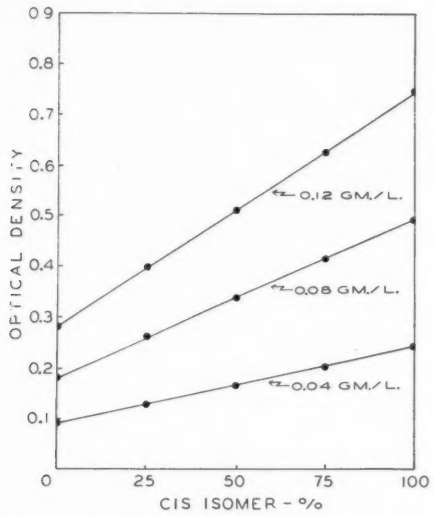

FIG. 1. *Effect of cis-trans ratio on the optical density of azobenzene solutions in acetone at 4400Å.*

Determination of the Rate of Isomerization

The organic solvents were supplied by Brickman and Co., Montreal. They were of reagent grade and were further dried and redistilled before using.

The water used as solvent was of conductance grade and had a pH of 6.3.

A solution of *cis*-azobenzene, usually at a concentration of 0.08 gm. per liter, was made up in the solvent being studied. Samples, contained in 1-oz., amber colored bottles, fitted with screw caps, were placed in a thermostat and withdrawn at measured time intervals. The per cent conversion was determined by analyzing the samples as previously described. Where limited quantities of a solvent were available, higher concentrations of azobenzene were used, and the samples diluted with acetone to 0.08 gm. per liter before analysis.

Experimental Results

Following the above procedure, the rate of the isomerization reaction was determined in 16 pure solvents at three temperatures corresponding approximately to 44°, 60°, and 76°C. The kinetic data for a typical solvent, nitro-

benzene, are reproduced in full in Figs. 2 and 3. The linearity of the plots of log (% *cis*) against time indicates that the reaction is consistently first order.

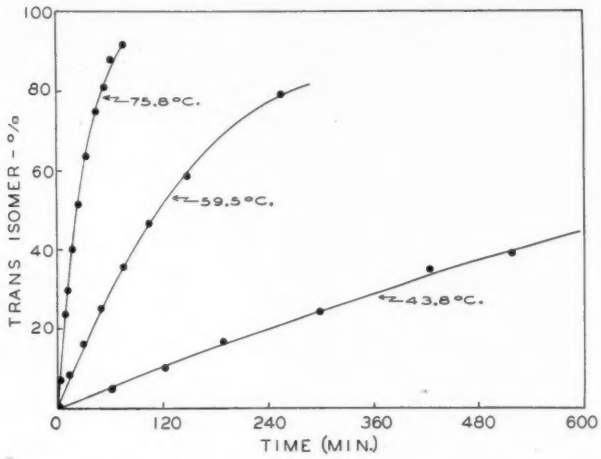

FIG. 2. *Rate of isomerization of azobenzene in nitrobenzene at various temperatures.*

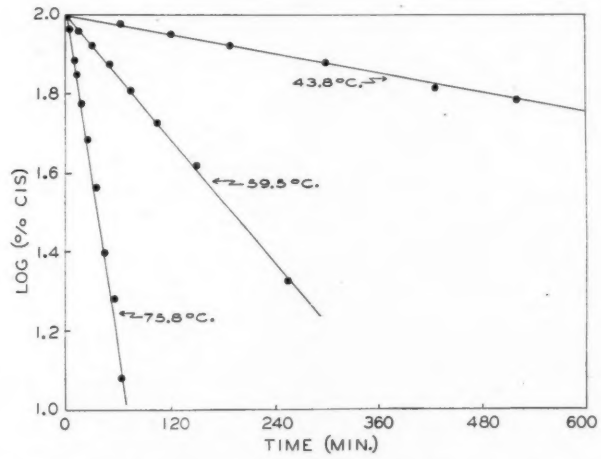

FIG. 3. *Isomerization of azobenzene in nitrobenzene. Log (% cis) vs. time.*

First order rate constants, k, calculated from the slopes of the plots of log (% *cis*) against time were found to be independent of concentration. When log k was plotted against $1/T$, excellent Arrhenius lines were obtained for each of the solvents. The activation energies, E, and the frequency factors, A, of the reaction in the different solvents, were calculated from the slopes of these

lines, using the Arrhenius equation. The results are listed in Table I. The rates are estimated as being accurate to within 2% and most of the activation energies to within 100 cal. per mole.

TABLE I

ISOMERIZATION OF AZOBENZENE IN VARIOUS SOLVENTS
SUMMARY OF KINETIC DATA

Solvent	Temp., °C.	Rate, min.$^{-1}$	Log k	E, kcal./mole	Log A
Heptane	43.8	0.001415	$\bar{3}$.151	22.8	12.877
	59.5	0.00790	$\bar{3}$.897		
	75.8	0.0392	$\bar{2}$.593		
Toluene	43.9	0.001089	$\bar{3}$.037	23.2	13.031
	59.5	0.00619	$\bar{3}$.791		
	76.8	0.0342	$\bar{2}$.532		
Benzene	43.9	0.001078	$\bar{3}$.032	23.3	13.101
	59.5	0.00603	$\bar{3}$.781		
	76.9	0.0359	$\bar{2}$.555		
Nitrobenzene	43.8	0.001035	$\bar{3}$.015	23.5	13.227
	59.5	0.00599	$\bar{3}$.777		
	75.8	0.0311	$\bar{2}$.493		
Decañol	43.8	0.001018	$\bar{3}$.008	23.15	12.946
	59.5	0.00570	$\bar{3}$.756		
	76.9	0.0320	$\bar{2}$.505		
Hexanol	43.9	0.000887	$\bar{4}$.948	23.7	13.300
	59.5	0.00514	$\bar{3}$.710		
	78.0	0.0336	$\bar{2}$.527		
Ethyl acetate	43.9	0.000789	$\bar{4}$.897	23.2	12.918
	59.5	0.00455	$\bar{3}$.658		
	75.3	0.0225	$\bar{2}$.352		
Butanol	43.9	0.000788	$\bar{4}$.896	23.95	13.387
	59.5	0.00454	$\bar{3}$.657		
	77.5	0.0297	$\bar{2}$.473		
Dioxane	43.9	0.000797	$\bar{4}$.901	23.6	13.154
	59.5	0.00451	$\bar{3}$.654		
	76.7	0.0269	$\bar{2}$.430		
Aniline	43.9	0.000742	$\bar{4}$.870	24.0	13.407
	59.5	0.00435	$\bar{3}$.637		
	76.8	0.0267	$\bar{2}$.427		
Acetone	43.8	0.000673	$\bar{4}$.828	23.7	13.188
	59.5	0.00396	$\bar{3}$.598		
	76.0	0.0223	$\bar{2}$.348		
Ethanol	43.9	0.000645	$\bar{4}$.810	24.3	13.565
	59.5	0.00376	$\bar{3}$.575		
	77.1	0.0254	$\bar{2}$.404		
Nitromethane	43.9	0.000548	$\bar{4}$.739	24.2	13.425
	59.5	0.00335	$\bar{3}$.525		
	76.8	0.01943	$\bar{2}$.288		
Methanol	43.8	0.000489	$\bar{4}$.689	24.75	13.718
	59.5	0.00294	$\bar{3}$.468		
	76.9	0.01935	$\bar{2}$.287		

TABLE I—*Concluded*

Solvent	Temp., °C.	Rate, min.$^{-1}$	Log k	E, kcal./mole	Log A
Acetonitrile	43.9	0.000486	$\bar{4}$.686	23.9	13.163
	59.5	0.002845	$\bar{3}$.453		
	75.3	0.01491	$\bar{2}$.174		
Water	43.8	0.000233	$\bar{4}$.367	23.0	12.228
	59.5	0.001315	$\bar{3}$.118		
	76.0	0.00682	$\bar{3}$.834		

The significance of the experimental activation energy, E, in solution reactions has been questioned, since it has been found that in some reactions E varies with the temperature (17, 25). This effect has been variously interpreted (17, 25) but the existing evidence indicates that it is significant only with ionic reactions. No appreciable variation of E with temperature has been observed with most molecular reactions, and there is certainly no evidence for it in the *cis–trans* isomerization of azobenzene, where the Arrhenius lines show no noticeable deviations from linearity in a temperature range of more than 30°C.

To determine the effect of continuous variation of the solvent medium, the kinetics of the isomerization reaction were also investigated in a number of mixed solvents. Heptane–ethanol, water–ethanol, and heptane–benzene mixtures, with ratios covering the entire composition range, were used. The rates at 59.9°C. are plotted as functions of the solvent composition in Fig. 4. The

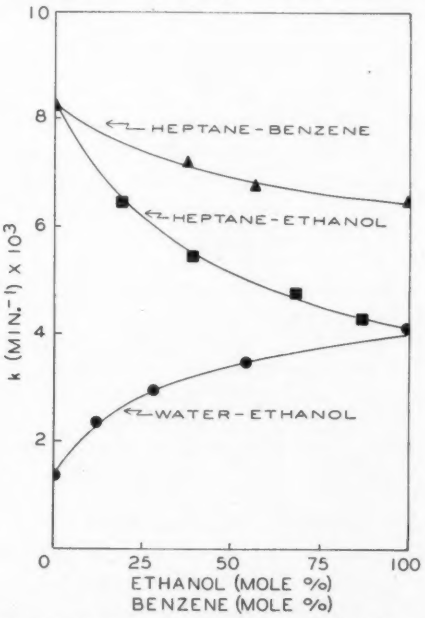

FIG. 4. *The cis-trans isomerization of azobenzene in various solvent mixtures.*

variation of E with solvent composition is described in Fig. 5. It might appear at first sight that there should be a maximum in the water–ethanol curve at 12 mole % ethanol. However, the evidence for this rests largely on one of the points, that for 11.8 mole % ethanol. Since the deviation of this point from the curve as drawn in Fig. 5 is only 150 cal. per mole, it may represent a possible experimental error, and the inclusion of a maximum in the curve was not considered justified.

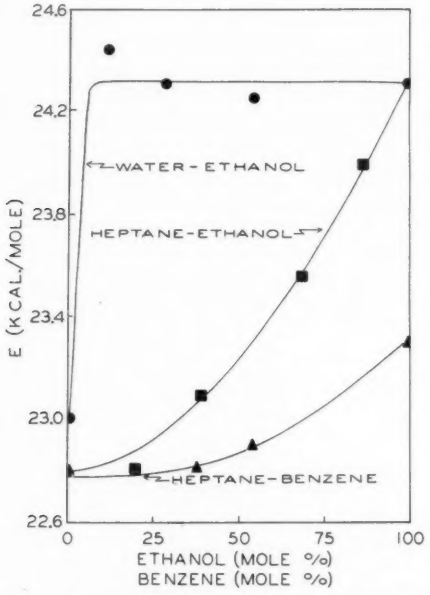

FIG. 5. *The variation of E with solvent composition.*

Discussion

The kinetic data for the *cis–trans* isomerization of azobenzene in the various pure solvents has been summarized in Table I. The solvents used include a representative variety of chemical types. It may be seen that the rate of the reaction (at 59.5°C.) varies from 0.00790 min.$^{-1}$ in heptane to 0.001315 min.$^{-1}$ in water, an approximately sixfold variation. The corresponding activation energies range from 22.8 to 24.75 kcal. per mole. An attempt is made below to account for these variations in the light of the theory outlined in the introduction.

To test the applicability of Equation (9) to these results, the internal pressures of all the solvents were calculated. The heats of vaporization (ΔH_{vap}), and molar volumes V, of the liquids were obtained from the International Critical Tables and the Landolt–Börnstein Tables. Where the value of ΔH_{vap}

for a solvent at 60°C. was not available, it was estimated by interpolation from data at other temperatures. The energy of vaporization, ΔE_{vap}, was then calculated using the approximate relation,

$$\Delta E_{vap} = \Delta H_{vap} - RT.$$

The internal pressure, P'_S, of each solvent was calculated (6) using the equation,

$$P'_S = \frac{(\Delta E_{vap})_S}{V_S}. \tag{13}$$

In Fig. 6, E is plotted as a function of $(P'_S)^{1/2}$. It is seen that the points for the different solvents fall on a straight line. This is in agreement with the relation expressed in Equation (9).

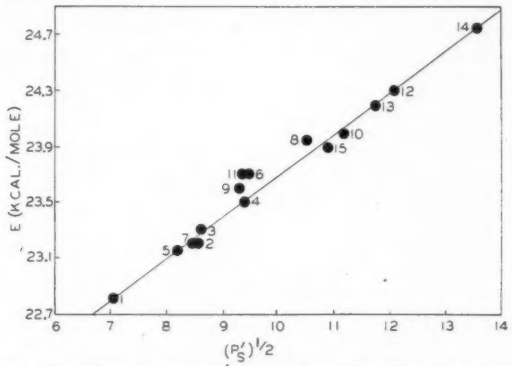

FIG. 6. *The relation between E and $(P'_S)^{1/2}$ for the isomerization of azobenzene in different solvents.**

Water is the only solvent for which the data do not correspond to this relation. The activation energy for the reaction in water is much lower than would be anticipated on the basis of its internal pressure, and the point corresponding to water does not appear in Fig. 6. A possible explanation for this is suggested by the results of experiments of Hartley (10), who found that, even in pure water, the H^+ ion concentration is sufficient to cause 25% of the isomerization to occur by an H^+ catalyzed mechanism, which probably has a considerably lower activation energy than the uncatalyzed reaction. Since the isomerization in water proceeds partly by a different mechanism from that in other solvents, correlations such as that indicated in Fig. 6 would hardly be expected to apply to it. Consequently it is omitted from this and subsequent discussions.

The plot in Fig. 6 is expressed by the equation,

$$E = 20.69 + 0.2994\ (P'_S)^{1/2}. \tag{14}$$

The activation energy for the reaction in each solvent was calculated by inserting the corresponding value of (P'_S) in this equation. The average deviation between calculated and experimental values of E is only 53 cal. per mole or 2.7% of 1950 cal. per mole, the range over which E varied in the group of solvents used. This is well within the experimental error of E.

**Figs. 6, 7 and 8 Legend. 1. Heptane. 2. Toluene. 3. Benzene. 4. Nitrobenzene. 5. Decanol. 6. Hexanol. 7. Ethyl acetate. 8. Butanol. 9. Dioxane. 10. Aniline. 11. Acetone. 12. Ethanol. 13. Nitromethane. 14. Methanol. 15. Acetonitrile.*

The slope of the line in Fig. 6 is 299.4 (cal. per cc.)$^{1/2}$. A comparison with Equation (9) gives,

$$2\ V_X[(P'_X)^{1/2} - (P'_{M*})^{1/2}] = 299.4\ (\text{cal./cc.})^{1/2}. \qquad (15)$$

By the use of this equation the internal pressure of the activated complex, P'_{M*}, may be calculated from a knowledge of the internal pressure, P'_X, and the molar volume, V, of the reactant. These data are not available for azobenzene, but reasonable values may be assumed as a first approximation, giving an estimate of at least the relative value of P'_{M*}.

Thus the molar volume of *cis*-azobenzene is assumed to be 200 cc, (corresponding to a density of 0.92 gm. per cc.) and its internal pressure is taken as 100 cal. per cc. (most aromatic compounds have internal pressures of this order). Inserting these values in Equation (15), the internal pressure of the activated complex, P'_{M*}, is calculated to be 85.5 cal. per cc. or about 15% smaller than that of the reactant.

The dipole moment of the activated complex is presumably intermediate between the dipole moment of *cis*-azobenzene (3.0 Debye units) and that of the trans *isomer* (zero) (11). In view of the general tendency of the internal pressure to decrease with decreasing polarity (3), it might be anticipated that the internal pressure of the activated complex would be smaller than that of the reactant, in agreement with the result just obtained.

The comparatively small difference between the internal pressures of the reactant and activated complex is also to be expected, since they are merely different forms of the same molecule. This is true for most unimolecular reactions, and would account for the small solvent effect usually observed with these reactions (7).

Log A is plotted as a function of E in Fig. 7. The linear relation observed is in agreement with Equation (11). The equation of the line is

$$\text{Log } A = 3.13 + 0.428\ E. \qquad (15)$$

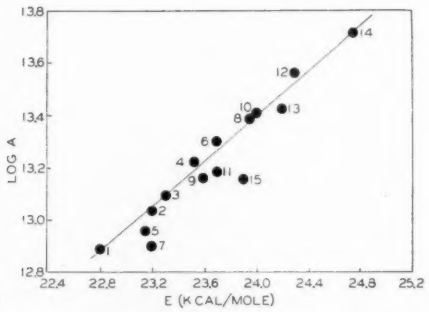

FIG. 7. *The relation between log A and E for the isomerization of azobenzene in different solvents.**

**See footnote on page 151.*

The average deviation between the values of log A calculated from this relation and the corresponding experimental values is 0.047, or 5.5% of the range over which log A varied in the groups of solvents considered.

The data for eight solvents, nitrobenzene, decanol, ethyl acetate, dioxane, acetone, ethanol, nitromethane and acetonitrile, show deviations in excess of 5% of this range, which may be taken as a reasonable estimate of the experimental error. Further examination reveals that, with the exception of dioxane, these have in general the highest dipole moments in the group of solvents used. Since *cis*-azobenzene itself has a dipole moment of 3, it would be expected that in highly polar solvents, there would be marked orientation effects and deviations from the simple behavior indicated by Equation (10) would be likely to occur.

Comparison of Equations (11) and (15) indicates that,

$$\frac{\rho_X}{2.303} = 4.28 \times 10^{-4} \text{ cal.}^{-1} ,$$

where ρ_X was previously defined by Equation (10). Thus where x now denotes azobenzene,

$$\rho_X = 9.85 \times 10^{-4} \text{ cal.}^{-1}$$

Using Equation (10), Evans and Polanyi (4) have determined the values of ρ for a large variety of systems from heats and entropies of solution. The values they found range from 4×10^{-4} to 8×10^{-4}. The value of 9.85×10^{-4} determined above from the relation between log A and E is of the same order of magnitude. This agreement would be expected if the considerations on the basis of which Equation (11) was derived are valid. It serves as an interesting example of the correlation between thermodynamic and kinetic phenomena implied in the Eyring theory.

The deviations from Equation (11), discussed above, are brought out even more clearly by the plot of log k against $(P'_S)^{1/2}$ shown in Fig. 8. The majority

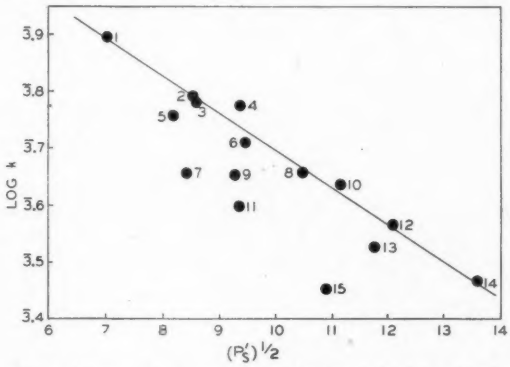

FIG. 8. *The relation between log k and E for the isomerization of azobenzene in different solvents.**

**See footnote on page 151.*

of the points are seen to lie fairly close to a straight line, as called for by Equation (12). The points for the polar solvents, previously noted, again show marked discrepancies from this relation. This would be expected, as it can be shown (14) that for systems in which the intermolecular forces are predominantly polar the dielectric constant, D, of the solvent rather than its internal pressure, determines the rate of the reaction. In very highly polar systems, a linear relation between $\log k$ and $\frac{D-1}{2D+1}$ has been found to prevail. For systems in which the forces are predominantly nonpolar the linear relation between $\log k$ and $(P'_S)^{1/2}$ is seen to apply well. However, for systems of intermediate polarity, as exemplified by azobenzene in the group of solvents previously listed, neither of these relations applies and no satisfactory quantitative treatment of the solvent effect on reaction rates has been achieved to date.

Figs. 4 and 5 show how the rate and activation energy of the isomerization reaction vary with the compositions of the various solvent mixtures. A quantitative correlation of k and E with solvent properties such as has been achieved with the pure solvents is impossible, since little is known about the internal pressures of liquid mixtures. In addition, it is likely that these solutions are not microscopically homogeneous, but, that in a mixed solvent, azobenzene is preferentially surrounded by the component in which it is more readily soluble. This is in fact indicated by the shapes of the curves in Fig. 4. In each of these the maximum slope occurs on the initial addition of the better solvent to the poorer one. (Azobenzene is far more readily soluble in ethanol and in benzene than in water and heptane.) Over most of the composition range, the rate of the reaction is closer to its value in the better solvent.

The evidence from the heptane–benzene system is particularly convincing. The internal pressure of an equimolar solution of heptane and benzene has been determined (26), and its value found to be somewhat closer to the internal pressure of benzene. Examination of the heptane–benzene curve in Fig. 4 reveals, however, that the rate of the isomerization in a solvent of this composition is very much closer to the rate in benzene; this indicates that the azobenzene molecules are preferentially surrounded by the better solvent, benzene.

These conclusions are not borne out by the heptane–benzene and heptane–ethanol curves shown in Fig. 5, where it is seen that the variation of the activation energies with solvent composition does not parallel that of the rates (Fig. 4). This indicates that the relation between E and A for the reaction in the mixed solvents is different from the relation for the pure solvents shown in Fig. 4. This is to be expected, since the relative tendencies of the reactant and activated complex molecules to be preferentially surrounded by one of the components of a mixed solvent will be different. Thus, a solvent mixture of a given over-all composition would in fact correspond to a different effective

solvent for the reactant and activated complex respectively. This would result in variations in E and A not observed with pure solvents, and makes the interpretation of the kinetic results in mixed solvents very difficult.

The results for the water–ethanol system shown in Fig. 5 are of particular interest. It is seen that the activation energy fails to fall off toward its value in water over most of the composition range. This is in keeping with the suggestion previously made, that the abnormally low activation energy of the reaction in water is due to H^+ ion catalysis. In the presence of ethanol the H^+ concentration would be considerably reduced and the activation energy correspondingly higher.

Acknowledgment

Grateful acknowledgment is made to the Committee on Research, McGill University, for financial assistance in the preparation of this manuscript.

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ON THE SOLUBILITY OF THORIUM NITRATE TETRAHYDRATE AND URANYL NITRATE HEXAHYDRATE IN ORGANIC SOLVENTS[1]

By Charles C. Templeton[2] and Norris F. Hall

Abstract

The values reported by Yaffe for the solubilities of thorium nitrate tetrahydrate and uranyl nitrate hexahydrate in various organic solvents are compared with those previously reported by Templeton and Hall, the former being much lower than the latter. Some of the accessory experiments of Templeton and Hall are here presented in support of the position that their values more closely correspond to equilibrium than those of Yaffe.

Yaffe (3) has recently published solubility data for thorium nitrate tetrahydrate in various organic solvents which differ greatly from the previously published results of Templeton and Hall. (2) In order to facilitate the proper evaluation of these differences, it now seems appropriate to present in detail the evidence which convinced Templeton and Hall that their systems had actually reached equilibrium—data which received only passing mention in their paper.*

Data

In both studies substantially equivalent materials and methods of analysis were used. By using the densities of the pure solvents, Yaffe's data, expressed as grams of thorium nitrate tetrahydrate per 100 ml. of *solvent*, may be converted to the basis used by Templeton and Hall, grams of thorium nitrate per 100 gm. of *solution*. This has been done in Table I for the five solvents which

TABLE I

Solubilities of thorium nitrate tetrahydrate in organic solvents

Solvent	Grams thorium nitrate per 100 gm. of solution	
	Yaffe 20° ∓ 0.5°C.	Templeton and Hall 25° ∓ 0.05°C.
Diethyl ether	16.7	42.8
Isoamyl alcohol (Isobutylcarbinol)	23.4	37.8
Methylisobutyl ketone	21.2	42.2
Methyl-*n*-amyl ketone	14.9	36.7
Diisopropyl ketone	6.6	20.8

[1] *Manuscript received November 21, 1949.*
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin, U.S.A.

[2] *Present address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.*

* *All the results in this communication and in the 1947 paper are taken from the thesis submitted by C. C. Templeton to the Graduate Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Master of Science, April, 1947.*

were included in both studies. Since Yaffe did not determine the densities of any of his solutions, no better method of conversion is possible. Hereafter all solubilities will be expressed as grams of thorium nitrate per 100 gm. of solution. Templeton and Hall (2) determined their solubilities by weighing a solution sample in a covered platinum crucible, and igniting directly to thoria.

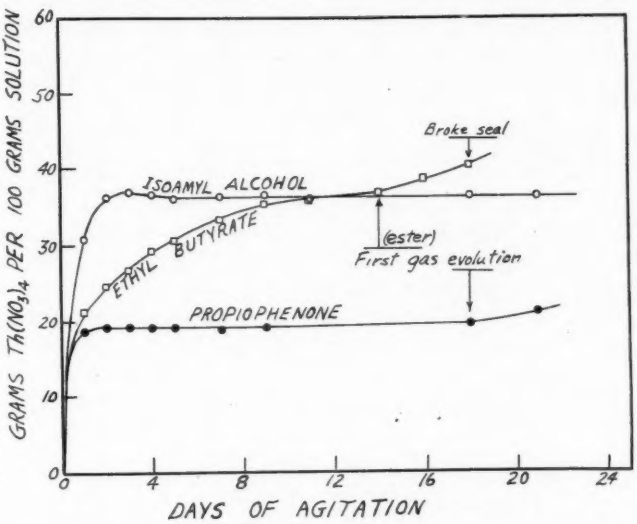

FIG. 1. *Composition of solutions of thorium nitrate tetrahydrate in organic solvents as a function of agitation time at 25°C.*

To justify the comparison of solubilities at temperatures which differ by 5°, the following data are presented. All agitation was end over end at 30 r.p.m. for samples in 6-in. test tubes.

(1) Sample 01, in isoamyl alcohol was agitated for 21 days at 25° + 0.05°C., reaching a solubility of 36.17 (see Fig. 1). For the following three days it was agitated at 35° ∓ 0.1°C., the final solubility being 36.28.*

(2) Sample 24, in methyl-*n*-amyl ketone, when four months old and just following four days of agitation at 25°C. had a solubility of 36.48. After standing another month, and immediately after four days of agitation at 35°C., the solubility was 36.55.

(3) Sample 26, in methyl-*n*-hexyl ketone with the same life history as sample 24, had a solubility of 31.12 at 25°C. and 31.05 at 35°C.

From these data it should be apparent that equilibrium differences due to temperature do not explain the incompatibilities in Table I.

** The 5% difference in the solubilities in isoamyl alcohol as listed here and in Table I is due to the use of different lots of "practical" grade solvent. Both workers say they used "practical grade or better"; however, this is not enough to explain the deviations in Table I.*

In Fig. 1 are given the variations in solubilities as a function of time for solutions of thorium nitrate tetrahydrate in isoamyl alcohol, propiophenone, and ethyl butyrate, which were agitated at 25° ∓ 0.05°C., the agitation beginning immediately after mixing and lasting for about 20 days. This is the chief evidence which convinced Templeton and Hall (*a*) that five days of constant agitation were sufficient for attaining equilibrium for alcohols and ketones, and (*b*) that equilibrium could not be reached in the case of esters; i.e., that the concentration could be increased continually until the entire system solidified. It may also be noted that in *every* case Templeton and Hall agitated their solutions for five days, whereas Yaffe indicates a minimum of one day and a maximum of four days. Further, for five solvents, Templeton and Hall determined the solubility from duplicate determinations on either three or four separately mixed systems.

In Table II are listed previously unpublished solubilities of uranyl nitrate hexahydrate in isoamyl alcohol, methyl-*n*-hexyl ketone, and ethyl butyrate which the authors determined after agitating the solutions for five days at 25° ∓ 0.05°C. Also some of Yaffe's data are included for comparison.

TABLE II

SOLUBILITIES OF THORIUM NITRATE TETRAHYDRATE AND URANYL NITRATE HEXAHYDRATE IN ORGANIC SOLVENTS

Solvent	Worker	Gm. $Th(NO_3)_4$ per 100 gm. solution	Molality (*) $Th(NO_3)_4$	Gm. of $UO_2(NO_3)_2$ per 100 gm. solution	Molality (*) $UO_2(NO_3)_2$
Isoamyl alcohol (Isobutylcarbinol)	T. and H. 25°C. Yaffe 20°C.	37.8 23.4	1.27 0.64	44.1 32.2	2.01 1.20
Methyl-*n*-hexyl ketone	T. and H. 25°C.	31.06	0.94	38.6	1.59
Methyl-*n*-amyl ketone	Yaffe 20°C.	14.9	0.364	35.4	1.39
Ethyl butyrate†	T. and H. 25°C.	31.0	0.935	40.6	1.74
Butyl acetate	Yaffe 20°C.	5.95	0.132	34.1	1.31

* *Moles of anhydrous nitrate per 1000 gm. of solvent plus water.*
† *Agitated for five days, but still not yet in equilibrium.*

Discussion

In Table I Yaffe's values for thorium nitrate tetrahydrate are seen to be generally about one-half of those of Templeton and Hall. It may be verified in the original papers that Yaffe's data for thorium nitrate tetrahydrate in *n*-amyl and capryl alcohols are similarly far below those of Templeton and Hall for *n*-butyl and *n*-hexyl alcohols. In Table II Yaffe's 20°C. value for uranyl nitrate hexahydrate in isoamyl alcohol is only three-fourths that of Templeton

and Hall at 25°C., and for the uranyl nitrate hexahydrate solubilities in the esters and ketones cited, Yaffe's values are again much lower, if one takes into account the molecular weights and structures of the solvents. However, there is not as much evidence for neglecting the temperature dependence in the uranyl nitrate hexahydrate case as there is in the thorium nitrate tetrahydrate case.

Either a good many of Yaffe's solutions were far below saturation, or those of Templeton and Hall were greatly supersaturated. In view of the slow velocity of solution of these systems and the truly steady states exhibited by the alcohol and ketone in Fig. 1, the authors believe that almost all of Yaffe's values for thorium nitrate tetrahydrate are very low. Considering that the thorium nitrate content of solutions in ethyl butyrate continually increases with agitation until the pressure of evolved gases breaks loose the cemented cork on the test tube, together with similar behavior for other esters, Templeton and Hall stated clearly their opinion that equilibrium solubilities could not be attained in esters by agitation. However, Yaffe later published data presented as being the equilibrium solubilities of these nitrates in a long list of similar esters. It is the authors' opinion that Yaffe didn't shake his systems long enough; some of them were given only 24 hr. It is indeed unfortunate that, in a separate column of his tables, Yaffe did not indicate these times of agitation, so that the data could now be sorted as to apparent validity.

How much of the disagreement may be attributed to the fact that both sets of data were determined with the use of practical grade solvents in many cases? The authors recognize that this will cause variations from the solubilities in the pure solvents (see footnote on page 157), but reject it as being the main cause of the discrepancy. It must be remembered that we are comparing solubility values which were determined in the same manner (except for intensity of agitation and a five degree difference in temperature) for solvents of the same general range of purity, not a value determined for a practical grade solvent with one determined for a highly purified solvent. Since over 70 solvents were included in each study, and these were used in the condition in which they were purchased, in any given case the question of which person had the purer solvent would be a matter of essentially random chance. Surely, then, if these impurities were the determining cause of the disagreement, some of Yaffe's values should be higher, as well as lower, than those of Templeton and Hall. Yet in *all* cases Yaffe's values are much the lower. Consequently we feel obliged to attribute the regular and systematic discrepancy to some cause other than these impurities.

Cheylan (1) states that after saturating anhydrous diethyl ether with thorium nitrate tetrahydrate and filtering off a slight amount of insoluble basic salt, a solution results which contains 36.9 gm. of thorium nitrate tetrahydrate per 100 cc., or 32.1 gm. of thorium nitrate per 100 cc. This was presumably done at ordinary room temperature. The density of the solution being lacking, this value cannot be calculated to the basis used in Table I. However, inspec-

tion of Table I will show Cheylan's result to be much more in line with that of Templeton and Hall than that of Yaffe.

The fortunate aspect of the situation is that one reaches about the same correlations between solvent power for these nitrates and the molecular structure of the solvent, regardless of whether equilibrium is reached, provided that all the solutions are subjected to roughly the same treatment. Thus, approximately equivalent conclusions were reached in both studies, although Templeton and Hall more definitely connected the solubility with the oxygen-containing groups of the solvent, by relating increased steric hindrance around that group with decreased solvent ability. One reason for presenting the new uranyl nitrate hexahydrate solubilities which are contained in Table II is to confirm the additional conclusion of Yaffe that uranyl nitrate hexahydrate seems to be always more soluble than thorium nitrate tetrahydrate.

Acknowledgment

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THE NORMAL BOILING POINTS AND OTHER PHYSICAL PROPERTIES OF STRONG SOLUTIONS OF SILVER NITRATE AND OF AMMONIUM NITRATE[1]

By Alan N. Campbell and Elinor M. Kartzmark[2]

Abstract

The present paper is a record of certain of the physical properties of solutions of silver nitrate and of ammonium nitrate, which were made by us in connection with our work on conductance. Some of these properties were actually used in calculations, others not, but they are collected here in their entirety. The properties described are: (1) normal boiling point; (2) densities and partial molar volume of water in solution; (3) viscosities at different concentrations and temperatures, as compared with those of a typical nonelectrolyte, urea; (4) the temperature coefficient of fluidity compared with the temperature coefficient of conductance; (5) the distribution coefficient of acetic acid between ether and solutions of silver nitrate.

In connection with the work of a previous paper (4) on the conductances of strong solutions of silver nitrate and of ammonium nitrate, we determined or calculated several physical properties, and these data we subsequently discarded as having no bearing on the main problem. Since, however, these properties were determined with care, we now communicate our results, especially as some of them have an obvious value in thermodynamic calculations. These properties are:

1. Normal boiling point;
2. Densities and partial molar volume of water in all solutions;
3. The viscosities at different concentrations and temperatures, as compared with those of a typical nonelectrolyte (urea), and with those of a typical weak electrolyte, acetic acid;
4. The temperature coefficient of fluidity compared with the temperature coefficient of conductance;
5. The distribution coefficient of acetic acid between ether and solutions of silver nitrate.

Experimental

Viscosity

These determinations were made in the usual way, using an Ostwald viscometer calibrated with water: no correction was made for kinetic energy. All

[1] *Manuscript received September 29, 1949.*
Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.
[2] *Holder of a Summer Bursary under the National Research Council of Canada, 1948 and 1949.*

determinations of viscosity and density were made in the thermostat used for conductance measurements, at a temperature of 25.0 ± 0.01°C. By way of comparison the viscosities of a typical nonelectrolyte, urea, and of a typical weak electrolyte, acetic acid, of corresponding concentrations were also determined.

Densities and Partial Molar Volumes

Solutions were all made up by weighing, so as to be independent of graduated apparatus, and densities were determined in a Weld pyknometer. (Cf. (4) for full details of our technique.) The partial molar volume of the solvent water, in solutions of silver nitrate and of ammonium nitrate, was obtained by plotting molar volume of the solution against mole fraction. (Cf. Lewis and Randall, (5, p. 38.)

Distribution Coefficient

It was thought that some measure of the activity of the solvent might be obtained by investigating the variation of the distribution ratio of acetic acid between ether and water and between ether and different solutions of electrolyte. Acetic acid is associated in ethereal solution and we attempted to overcome the variation in the simple distribution ratio which this would cause by using always the same total weight (1 ml. of glacial acetic acid) and the same volumes of ether and of solution. Ninety milliliters of ether and 90 ml. of silver nitrate solution, together with 1 ml. of glacial acetic acid, were stirred in the thermostat for 24 hr., after which 25 ml. portions of each layer were titrated with standard baryta. We were forced to use acetic acid, rather than succinic acid, because of the insolubility of silver succinate. We have evaluated both $K_1 = c_1/c_2$, where c_1 = concentration of acetic acid in solution of silver nitrate, c_2 = concentration of acetic acid in ether, and $K_2 = c_1/\sqrt{c_2}$. Neither of the two ratios is constant and constancy is not to be expected since the increasing concentration of electrolyte will affect considerably the activity of the solvent water.

Boiling Points of Solutions

In our quest for a ready method of obtaining the activity coefficients of the solvent water in electrolytic solutions, we turned to the boiling point. We had at our disposal the barostat used by Campbell and Dulmage in their work on the boiling points and vapor compositions of a three-liquid mixture (3). The boiling point apparatus of Scatchard (Cf. Campbell and Dulmage (3)) was used. Boiling points of very concentrated solutions were obtained by placing anhydrous salt in the inner chamber and a solution of moderate concentration in the outer. In this way the boiling point of a saturated solution was first obtained, and afterwards the boiling points of solutions progressively more

dilute. A sample of each solution was withdrawn for analysis as soon as the boiling point was read, except in the case of the saturated solution where the concentration was read off from the solubility isotherm. (Silver nitrate: Campbell and Boyd (2); ammonium nitrate: Millican, Joseph and Lowry (7).) Silver nitrate solutions were analyzed electrolytically (Cf. Campbell and Boyd (2).) and ammonium nitrate solutions by a modification of the Kjeldahl method described by Smith and Lennox (8). More dilute solutions were prepared before introduction to the apparatus but they were also analyzed, since the concentration changes during the attainment of equilibrium.

By the experimental technique described we were able to extend our measurements beyond 60 molal, in the case of silver nitrate, i.e., to such a concentration

TABLE I

BOILING POINTS. p = 760 MM.

Weight % solute	Molality	Mole fraction water	Boiling point, °C.
*A. Silver nitrate**			
1.61	0.10	0.998	100.055
13.59	0.92	0.984	100.735
25.77	2.04	0.964	101.400
33.50	2.97	0.950	101.795
41.44	4.17	0.930	102.310
47.33	5.29	0.913	103.105
54.52	7.06	0.887	103.85
56.64	7.69	0.879	103.91
65.92	11.39	0.830	105.18
66.77	11.83	0.825	105.48
70.04	13.76	0.802	106.30
77.39	20.15	0.734	108.6
82.36	27.48	0.669	111.1
85.14	33.72	0.622	113.6
90.55	56.40	0.496	122.3
92.14	69.01	0.446	134.1
B. Ammonium nitrate			
10.51	1.47	0.974	102.0
20.09	3.14	0.947	103.0
22.95	3.72	0.937	103.9
28.72	5.03	0.917	104.9
43.10	9.46	0.855	108.5
50.66	12.83	0.812	111.0
61.87	20.27	0.733	116.5
68.78	27.52	0.669	120.9
80.32	50.99	0.522	129.6
87.40	86.65	0.391	145.7

* *In the region of high concentration there are two concentrations of silver nitrate having the same boiling point but only one is realizable by our technique.*

that the mole fraction of the water was less than 0.5. It was not possible to extend the ammonium nitrate measurements up to saturation, because a saturated solution of ammonium nitrate has no boiling point, i.e., its vapour pressure is less than 760 mm. Table I contains the normal boiling points of silver nitrate solution and of ammonium nitrate solutions at various concentrations.

Table II contains the densities and partial molar volumes of water in solutions of silver nitrate and of ammonium nitrate.

TABLE II

DENSITIES OF SOLUTIONS OF SILVER NITRATE AND OF AMMONIUM NITRATE, AND PARTIAL MOLAR VOLUMES OF WATER IN THESE SOLUTIONS

Concentration		$d_4^{25°}$ m./ml.	Molar volume of solution	Partial molar volume of water in solution
Wt. % solute	Mole fraction			
A. Silver nitrate				
1.68	0.00178	1.0111	18.074	18.10 (pure water = 18.10)
14.96	0.0183	1.136	18.285	18.01
26.68	0.0371	1.273	18.563	17.98
36.22	0.0567	1.407	18.913	17.93
44.08	0.0771	1.542	19.254	17.91
50.58	0.0978	1.675	19.620	17.80
56.16	0.1195	1.806	20.014	17.66
61.07	0.1425	1.938	20.46	17.51
65.49	0.1674	2.069	20.99	17.45
71.59	0.2107	2.298	21.76	17.00
B. Ammonium nitrate				
0.80	0.00181	1.0002	18.120	18.10
7.75	0.01855	1.028	18.625	18.01
15.08	0.03941	1.059	19.245	18.01
21.99	0.05961	1.089	19.922	17.95
28.66	0.08287	1.119	20.683	17.95
34.77	0.1071	1.147	21.480	17.90
40.93	0.1348	1.187	22.397	17.84
46.80	0.1659	1.205	23.420	17.75
52.10	0.1965	1.233	24.484	17.64
56.63	0.2270	1.257	25.511	17.31
62.32	0.2711	1.284	27.113	17.05
68.49	0.3283	1.319	29.16	16.90

Table III contains the densities and relative viscosities of aqueous solutions of silver nitrate, of ammonium nitrate, of a typical weak electrolyte, acetic acid, and of a typical nonelectrolyte, urea, at various concentrations and temperatures. The viscosities are referred to water at 25° as unity.

TABLE III

DENSITIES AND VISCOSITIES OF SOLUTIONS OF SILVER NITRATE, OF AMMONIUM NITRATE, OF ACETIC ACID, AND OF UREA

Normality	Temperature, °C.	Density gm./ml.	Viscosity (water = 1.000)
A. Silver nitrate			
1.0	25.0	1.137	1.075
1.0	28.0	1.136	1.035
2.0	25.0	1.276	1.179
2.0	32.6	1.271	1.009
3.0	25.0	1.413	1.307
3.0	32.6	1.407	1.137
3.0	39.0	1.402	1.011
3.98	25.0	1.544	1.473
3.98	39.0	1.537	1.140
3.98	46.5	1.530	1.010
5.0	25.0	1.685	1.658
5.0	47.0	1.668	1.145
5.0	55.9	1.663	1.003
5.97	25.0	1.810	1.890
5.97	55.9	1.791	1.139
5.97	66.5	1.786	1.004
6.95	25.0	1.943	2.170
6.95	66.5	1.923	1.160
6.95	79.0	1.908	1.009
7.96	25.0	2.075	2.506
7.96	79.0	2.046	1.156
7.96	94.8	2.033	1.004
B. Ammonium nitrate			
0.100	25.0	1.0002	0.991
0.996	25.0	1.028	0.960
1.996	25.0	1.059	0.952
2.993	25.0	1.089	0.977
4.007	25.0	1.119	1.009
4.984	25.0	1.149	1.061
6.019	25.0	1.178	1.144
7.043	25.0	1.205	1.234
8.026	25.0	1.233	1.366
8.898	25.0	1.257	1.521
9.998	25.0	1.284	1.776
11.282	25.0	1.319	2.170
C. Acetic acid			
1.735	25.0	1.011	1.197
3.437	25.0	1.024	1.407
5.206	25.0	1.036	1.640
6.751	25.0	1.044	1.833
8.423	25.0	1.052	2.038
10.106	25.0	1.058	2.259
11.883	25.0	1.063	2.473
13.585	25.0	1.065	2.635
15.415	25.0	1.062	2.449
17.360	25.0	1.044	1.268

TABLE III—*Concluded*

Normality	Temperature, °C.	Density gm./ml.	Viscosity (water = 1.000)
D. Urea			
0.100	25.0	0.998	1.010
1.000	25.0	1.013	1.056
2.000	25.0	1.029	1.095
3.000	25.0	1.044	1.127
4.000	25.0	1.059	1.210
5.000	25.0	1.074	1.290
6.000	25.0	1.088	1.378
7.000	25.0	1.104	1.505
8.000	25.0	1.118	1.630
9.000	25.0	1.131	1.808
10.000	25.0	1.148	2.050

In Fig. 1 the viscosities at 25°C. of all solutions are plotted against mole fraction.

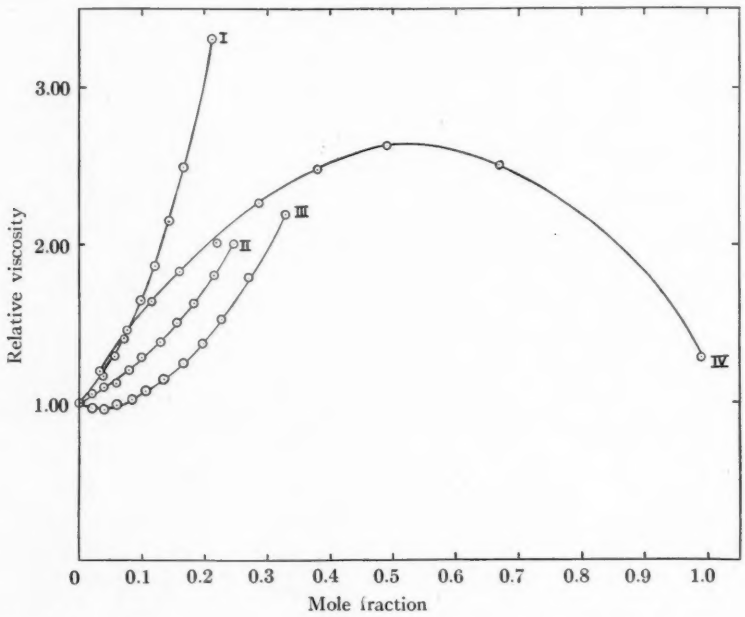

FIG. 1. *I. Silver nitrate* : *Viscosity (re. N/10 silver nitrate) vs mole fraction.*
II. Urea : *Viscosity (re. water) vs mole fraction.*
III. Ammonium nitrate : *Viscosity (re. N/10 ammonium nitrate) vs mole fraction.*
IV. Acetic acid : *Viscosity (re. water) vs mole fraction.*

In Fig. 2 equivalent conductances (of silver nitrate only), taken from a previous paper (4), and fluidities are plotted against temperature for different concentrations. Owing to lack of points, the curves are necessarily drawn as straight lines joining points. The same information is contained in Fig. 3 where the ratios $\phi_t/\phi_{25°}$ and $\Lambda_t/\Lambda_{25°}$ are plotted against temperature (6, p. 275).

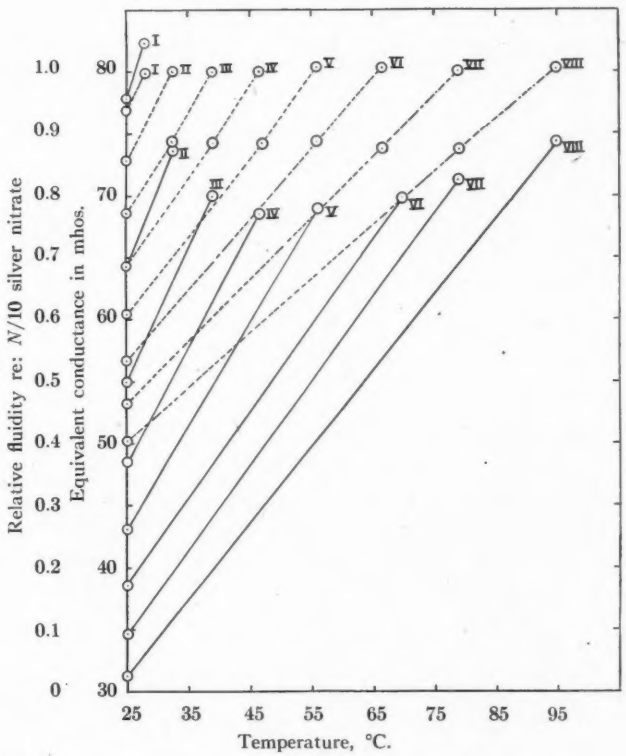

FIG. 2. ——— *Equivalent conductance vs. temperature*
– – – – – – *Fluidity vs. temperature (re: N/10 silver nitrate)*

I. 1.0 N	*V. 5.0 N*
II. 2.0 N	*VI. 5.97 N*
III. 3.0 N	*VII. 6.95 N*
IV. 3.98 N	*VIII. 7.96 N*

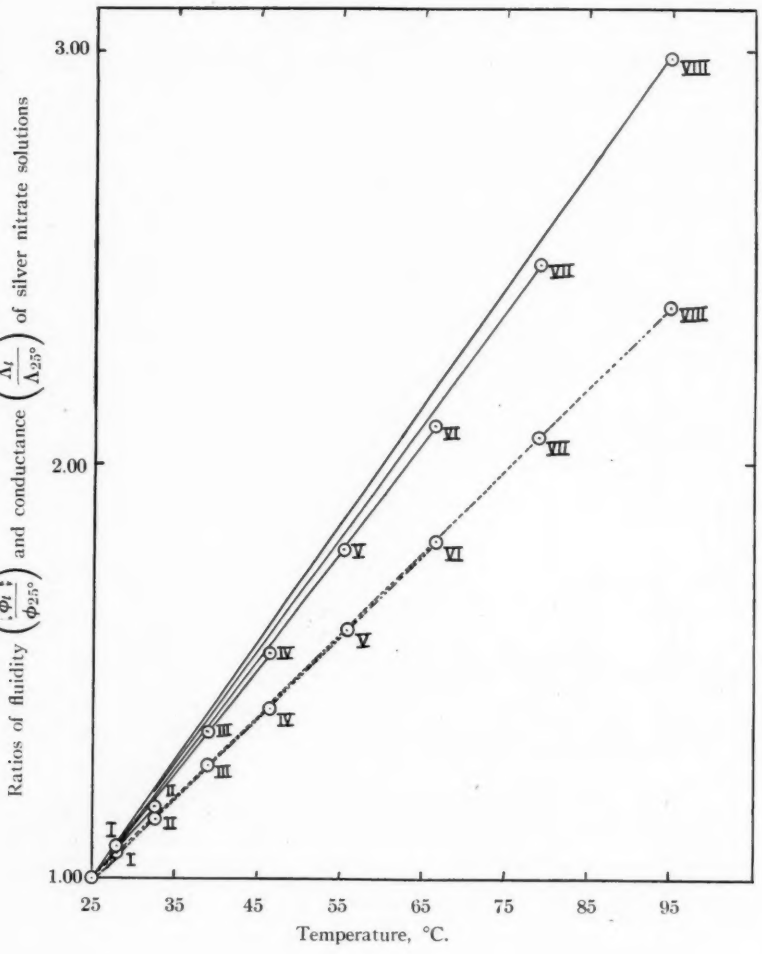

FIG. 3.

——— $\frac{\phi_t}{\phi_{25°}}$ — *I.* *1.0 N*; *II.* *2.0 N*; *III.* *3.0 N*; *IV.* *3.98 N*; *V.* *5.0 N*; *VI.* *5.97 N*; *VII.* *6.95 N*; *VIII.* *7.96 N*

- - - - - $\frac{\Lambda_t}{\Lambda_{25°}}$

Table IV contains the distribution ratio for acetic acid between ether and silver nitrate solutions.

TABLE IV

DISTRIBUTION RATIOS c_1/c_2 AND $c_1/\sqrt{c_2}$ OF ACETIC ACID BETWEEN ETHER AND SILVER NITRATE SOLUTIONS

Molarity of solution	c_1* (solution)	c_2* (ether)	$K_1 = c_1/c_2$	$K_2 = c_1/\sqrt{c_2}$
Water	0.128	0.056	2.27	8.54
0.100	0.130	0.058	2.24	8.62
1.001	0.138	0.0665	2.08	8.52
1.999	0.143	0.074	1.94	8.36
3.000	0.141	0.073	1.94	8.32
4.002	0.135	0.077	1.76	7.75
4.986	0.133	0.085	1.56	7.23
5.972	0.116	0.085	1.36	6.33
6.965	0.110	0.094	1.17	5.72
7.975	1.055	1.04	1.01	5.19
9.709	1.095	1.385	0.791	4.67

* *Moles per liter.*

Discussion of Results

No lengthy discussion of these purely experimental data is necessary. The relation between conductance, fluidity, and temperature is interesting. The plot of fluidity of silver nitrate solutions against temperature is almost a straight line, while that of viscosity (not given) is markedly convex to the axis of temperature, in accordance with the pronouncement of Bingham (1). The temperature coefficient of conductance is markedly less than that of the temperature coefficient of fluidity. Hence the effect of temperature on conductance is not merely that of increasing fluidity, either of water or of the solution as a whole.

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NOTES

The Synthesis of 3,3′-Methylene-C^{14}-*bis*(4-hydroxycoumarin)

Dicumarol, or 3,3′–methylene–*bis*(4-hydroxycoumarin), is the causative agent of the hemorrhagic disease of cattle known in agricultural practice as "sweet clover disease" (1). This compound is now produced on a commercial scale and is used clinically for the treatment of thrombosis. Quite obviously, C^{14}-labeled dicumarol would be of value in physiological investigations and a consideration of its synthesis indicates that radio-carbon may be very simply incorporated into the molecule of dicumarol by using radioactive formaldehyde.

The preparation of 3, 3′-methylene-C^{14}-*bis*(4-hydroxycoumarin) was effected by adding an aqueous solution of formaldehyde-C^{14} (21% formalin), obtained from the Oak Ridge National Laboratory (2), to an excess of 4-hydroxycoumarin in the form of a saturated aqueous solution, e.g., 5 mgm. of formaldehyde to 100 mgm. of 4-hydroxycoumarin in 200 cc. of water. The reaction mixture was allowed to stand at room temperature, with occasional shaking, for 48 hr. The precipitated dicumarol was then collected by filtration, washed with methanol, and crystallized from cyclohexanone. The yield of the crystalline product was 70 to 75% based on the formaldehyde-C^{14}. It melted alone, and on admixture with an authentic sample of dicumarol, at 288° to 290°C. Its diacetate derivative was prepared by treatment with acetic anhydride. The melting point of the diacetate was 250° to 252°C. with decomposition, which is in agreement with the behavior reported by Stahmann *et al.* (3).

The specific activity of the formaldehyde-C^{14}, according to the data supplied by the Oak Ridge National Laboratory, was 210 μc. per millimole. Hence, the 3,3′-methylene-C^{14}-*bis*(4-hydroxycoumarin) prepared from this formaldehyde should contain $210/336 = 0.625$ μc. of β activity per mgm.

Radioactive measurements, using an end-window type of Geiger–Müller counter with a scale of 128, indicated a specific activity of 6.0×10^4 counts per min. per mgm. dicumarol. This is in agreement with the calculated value if one assumes about 20 disintegrations per count; a not unreasonable assumption for the particular counter used in these experiments.

Experiments with mice and rabbits, using dicumarol labeled in the above mentioned manner, provide evidence that the liver constitutes the target organ for the action of dicumarol.

Acknowledgments

We are grateful to the United States Atomic Energy Commission for supplying formaldehyde-C^{14} and to the National Research Council of Canada for financial assistance.

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Note on the Solubility of Thorium Nitrate Tetrahydrate and Uranyl Nitrate Hexahydrate in Organic Solvents*

I am grateful to Mr. Templeton for submitting to me a prepublication copy of his note. I am pleased that the conclusions which we (1) drew are similar to those of Templeton and Hall (3), even though differences in the actual solubility data exist.

The question of attainment of equilibrium or supersaturation of solution is one which can, of course, be proved only by further experiments. However, I feel that this would be begging the question, since if precise solubility data were what were being sought, both Templeton and Hall's work and ours would be subject to a very serious criticism. The use of "Practical" grade chemicals without further purification can lead to very faulty conclusions since one is then dealing with a multicomponent system rather than a two or a three component one. For example, Templeton and Hall (2, footnote on page 157) find a 5% difference in the solubility of thorium nitrate tetrahydrate in isoamyl alcohol in two of their own experiments. This is undoubtedly correctly ascribed to their "use of different lots of practical grade solvent" (even though presumably obtained from the same manufacturer). That such a discrepancy can be further emphasized is well known. The solubility of salts in diethyl ether is greatly influenced by the presence of water, nitric acid, etc.

As a consequence of this, it is not surprising that our results differ from Templeton and Hall's. To quote from the introduction to our paper we set out "to establish a general relationship between the solubilities of the nitrates of some of the heavier elements in organic solvents and the molecular constitution of the solvent". I agree with Mr. Templeton's conclusions that this can be done without paying too much attention to the conditions of the experiment as long as the treatment is roughly identical. However, if one is looking for absolute solubility data, then the solvents and solutes must be subjected to a very rigorous purification procedure. This was not our intention and apparently not that of Templeton and Hall since on page 1442 of their original article they state that "no further purifications were made because of the desire to investigate a large number of solvents in a reasonable length of time".

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